Factors Affecting the Predicted Response of Fish Mercury Concentrations to Changes in Mercury Loading

Technical Report

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PRODUCT DESCRIPTION

A central issue for stakeholders interested in the potential benefits of reductions in mercury emissions to the environment is the corresponding response of fish mercury concentrations, both in magnitude and timing. EPRI developed the Dynamic Mercury Cycling Model (D-MCM), Version 2.0, to help understand and ultimately predict mercury cycling and bioaccumulation in lakes. This study examined the predicted response times of fish methylmercury (MeHg) concentrations to reductions in loading rates of inorganic mercury [Hg(II)] in four lakes. The study also examined several aspects of D-MCM that potentially impact these predicted response dynamics.

Results & Findings

This report describes studies of mercury cycling and bioaccumulation in four lakes, conducted using an updated version of EPRI's D-MCM. The four study lakes included Pallette Lake and Little Rock Reference Lake in Wisconsin, Lake 240 in Ontario, and Lake Barco in Florida. Model calibrations from previous applications were updated for each lake, followed by simulations of mercury load reduction scenarios that tested different model assumptions.

D-MCM predictions regarding the timing of fish mercury responses to changes in lake mercury loads were clearly sensitive to assumptions regarding sediment layer thickness and strongly bound mercury on particles. To date, D-MCM studies have typically assumed that the active sediment layer was 3 cm deep and that all of the inorganic Hg(II) bound to sediment solids was capable of instantaneous exchange. When these assumptions were applied to simulations of the four lakes involving mercury load reductions, fish mercury concentrations were predicted to require from 40 to 160 years to reach 90 percent of long-term steady-state values. When alternative assumptions were tested for Pallette Lake such that 90% of the inorganic Hg(II) on sediment particles was strongly bound and the sediment layer was reduced to a thickness of 1 cm, the predicted time for fish mercury concentrations to reach 90% of steady state decreased from 122 to 23 years.

The modeled response of fish mercury concentrations did not depend appreciably on whether the fish diet was primarily benthic or pelagic-based, using assumptions typically applied in previous studies. This finding was partly an outcome of the assumption that sediment methylation was the dominant modeled source of methylmercury to all four lakes. If methylmercury was alternatively supplied primarily from another source capable of responding more quickly than sediments (e.g., water column methylation), then the potential existed for fish with pelagic diets to respond more quickly than fish with benthic diets.

Challenges & Objectives

The simulations conducted in this study represent hypothesis testing and point out that the predicted responses of fish mercury concentrations to reductions in mercury loading are sensitive to assumptions about the thickness of the active sediment layer, the inclusion of strongly bound sediment inorganic Hg(II), and the primary site of methylation. There is insufficient scientific information, however, to support one group of assumptions over another. Furthermore, the model framework does not distinguish between newly received mercury and mercury that has been in the system for longer periods, such as years. Recent experimental evidence reveals that "new" mercury may be more available for methylation than older mercury. This factor also has the potential to impact the response dynamics of a lake to reductions in mercury loading. Such uncertainties underscore the fact that D-MCM should still be viewed as a research tool and should be applied cautiously as a predictive tool.

EPRI Perspective

Currently, researchers and regulators are in the midst of serious discussion concerning how mercury gets into food webs and which factors control the amount of mercury biotransferred to fish. The process of developing water quality criteria for mercury has only recently begun to consider benthic sources of methylmercury and variability among types of water bodies. The model simulations in this study reveal that assumptions about how mercury functions in sediments can greatly affect the outcome of model runs, specifically with respect to the amount of time it takes to see changes in fish mercury after a change in deposition rate. This reveals the need for further research before regulations are developed.

EPRI's D-MCM (product #1005424) is a joint product of the Institute's Mercury, Metals, and Organics in Aquatic Environments Program and the Air Toxics Health and Risk Assessment Program. Knowledge gained in this study will be used in future upgrades to D-MCM in 2004-2005. The model has also recently been used to simulate mercury cycling in aquatic mesocosms (EPRI report #1005171).

Keywords

Mercury
Methylmercury
Modeling
Bioaccumulation
Fish response

ABSTRACT

This report describes studies of mercury cycling and bioaccumulation in four lakes, conducted using an updated version of EPRI's Dynamic Mercury Cycling Model (D-MCM), Version 2.0. The study lakes included Pallette Lake and Little Rock Reference Lake in Wisconsin, Lake 240 in Ontario, and Lake Barco in Florida. Specifically examined were the predicted response times of fish methylmercury (MeHg) concentrations to reductions in loading rates of inorganic mercury [Hg(II)] in the lakes as well as several aspects of D-MCM that potentially impact these predicted response dynamics.

To date, D-MCM studies have typically assumed that the active sediment layer was 3 cm deep and that all of the inorganic Hg(II) bound to sediment solids was capable of instantaneous exchange. When these assumptions were applied to simulations of the four lakes involving mercury load reductions, fish mercury concentrations were predicted to require from 40 to 160 years to reach 90 percent of long-term steady-state values. When an alternative assumption was tested for Pallette Lake such that the sediment layer was reduced to a thickness of 1 cm, the predicted time to reach 90% of steady state decreased from 122 to 39 years. Furthermore, when the assumption that most of the inorganic Hg(II) on sediment solids (90%) was strongly bound was imposed in combination with a 1 cm sediment layer, the predicted time to reach 90% of steady state accelerated to 23 years. Clearly, D-MCM predictions regarding the timing of fish mercury responses to changes in lake mercury loads are sensitive to assumptions regarding sediment layer thickness and strongly bound mercury.

The modeled response of fish mercury concentrations did not depend appreciably on whether the fish diet was primarily benthic or pelagic for the base case scenarios tested in this study, with most of the methylmercury supply to the system occurring via a 3 cm deep sediment layer. Under such conditions, the predicted methylmercury concentrations in water, sediments, and all biota were essentially all dictated by the speed at which methylmercury production rates changed in sediments, regardless of whether fish diets were primarily benthic or pelagic. If methylmercury was alternatively supplied primarily from another source capable of responding more quickly than sediments (e.g., water column methylation), then the potential existed for fish with pelagic diets to respond more quickly than fish with benthic diets.

The simulations carried out in this study represent hypothesis testing and point out that the predicted responses of fish mercury concentrations to reductions in mercury loading are sensitive to assumptions about the thickness of the active sediment layer, the inclusion of strongly bound sediment inorganic Hg(II), and the primary site of methylation (e.g., water column versus a thin zone at the sediment interface versus the complete sediment compartment). There is currently insufficient scientific information, however, to support one group of assumptions over another. Furthermore, the model framework does not distinguish between newly received mercury and mercury that has been in the system for longer periods, such as years. Recent experimental

evidence reveals that “new” mercury may be more available for methylation than older mercury. This factor also has the potential to impact the response dynamics of a lake to reductions in mercury loading. Such uncertainties mean that D-MCM should still be viewed as a research tool and should be applied cautiously as a predictive tool at this point in its development.

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1
INTRODUCTION

This report describes the application of EPRI's Dynamic Mercury Cycling Model (D-MCM), Version 2.0, to explore the predicted dynamic response of fish mercury concentrations in four lakes to reductions in inorganic Hg(II) loading. The four lakes were Little Rock Reference Lake and Pallette Lake in Wisconsin, Lake 240 at the Experimental Lakes Area, Ontario, and Lake Barco, Florida. These lakes have been the subject of earlier field studies (e.g. Sellers *et al.,* 2001; Krabbenhoft *et al.,* 1998; Schofield, 1998; Sigler, 1998; Watras *et al.,* 1998; Harris *et al.,* in preparation; Gilmour and Riedel, *1995;* Hudson *et al.,* 1994; Watras *et al*., 1994, Hurley *et al.,* 1994). In association with these field studies, simulations were carried out with D-MCM to help understand mercury cycling and bioaccumulation in these lakes. The state of knowledge of mercury cycling continues to improve, and updates to some model processes and earlier calibrations were needed. There is also a long-term objective of obtaining a single model calibration that performs reasonably across a wide range of lake conditions. Currently however, manual tuning of some model constants is needed on a site-by-site basis to get reasonable calibrations for different sites. Under such conditions, a model can have value in a research capacity but cannot be used as a robust predictive tool.

During this study, efforts were made to reduce the number of model constants that need tuning on a site-by-site basis, and to examine some key model assumptions affecting the response times of fish mercury concentrations to changes in atmospheric mercury deposition. These factors included the fraction of irreversibly adsorbed inorganic Hg(II) onto sediment particles, the thickness of the active sediment layer, and benthic versus pelagic-based fish diets.

Section 2 of the report outlines the model study objectives. Sections 3 and 4 include an overview of D-MCM and the modeling approach used for this study respectively. Section 5 presents the relevant site conditions for the 4 study lakes, and modeling results are presented and discussed in Sections 6 and 7 respectively. Section 8 includes conclusions and recommendations.

2 OBJECTIVES

The overall objective of this study was to examine selected factors affecting the predicted response of fish mercury to changes in inorganic Hg(II) loading, and to reduce the number of model constants that needed adjustments on a site-by-site basis.

Specific objectives of this study were as follows:

- To update earlier model calibrations for the four lakes.
- To apply an updated version of D-MCM to four lakes to examine the effects of strongly (irreversibly) bound sediment inorganic Hg(II) on the predicted response times of fish methylmercury concentrations to reductions in mercury loading.
- To examine the what impact, if any, of pelagic versus benthic-based fish diets had on the predicted response of fish mercury to inorganic Hg(II) load changes.
- To examine the effect that the assumed active sediment layer thickness had on the ability of the modeled system to respond to load reductions.

3
OVERVIEW OF D-MCM

EPRI's Dynamic Mercury Cycling Model (D-MCM) is a Windows 95/98/NT™ based simulation model for personal computers (Tetra Tech, 2002). It predicts the cycling and fate of the major forms of mercury in lakes, including methylmercury, inorganic Hg(II), and elemental mercury. D-MCM is a time-dependent mechanistic model, designed to consider the most important physical, chemical and biological factors affecting fish mercury concentrations in lakes, including mercury loading rates. It can be used to develop and test hypotheses, scope field studies, improve the understanding of cause/effect relationships, examine responses to changes in mercury loading, and to help design and evaluate mitigation options.

An overview of the major processes in D-MCM is shown in Figure 3-1. These processes include inflows and outflows (surface and groundwater), adsorption/desorption, particulate settling, resuspension and burial, atmospheric deposition, air/water gaseous exchange, industrial mercury sources, in-situ transformations (e.g. methylation, demethylation, methylmercury photodegradation, inorganic Hg(II) reduction), mercury kinetics in plankton, and bioenergetics related to methylmercury fluxes in fish.

Model compartments include the water column, sediments and a food web that includes three fish populations. Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry deposition). Similarly, watershed/upstream loadings of inorganic Hg(II) and methylmercury are input directly as time-series data, not modeled. The user provides inputs for flow rates (surface and groundwater) and associated mercury concentrations, which are combined to determine the watershed mercury loads.

The food web consists of six trophic levels (phytoplankton, zooplankton, benthos, piscivore fish, omnivore fish and non-piscivore fish). Specific fish species can be selected. Fish mercury concentrations tend to increase with age, and are therefore followed in each year class. Methylmercury fluxes for individual fish were coupled to fish bioenergetics equations from Hewett and Johnson (1992) as described by Harris and Bodaly (1998). Fluxes were then scaled up to represent year classes and entire populations.

The predictive capability of D-MCM is evolving but is currently constrained by some scientific gaps. These knowledge gaps include the true rates and governing factors for methylation, demethylation, inorganic Hg(II) reduction, and site factors affecting methylmercury uptake at the base of the food web. Furthermore, the relationship between mercury loading and fish mercury concentrations is not known when considering loading changes on the order of magnitude that might occur due to emissions controls.

The development of D-MCM has been funded by EPRI and the Wisconsin Department of Natural Resources. It is an extension of previous mercury cycling models developed by Tetra Tech, including the original Macintosh-based MCM models developed during the EPRI-sponsored Mercury in Temperate Lakes Project in Wisconsin (Hudson *et al.,* 1994), and the subsequent steady state Regional Mercury Cycling Model (Tetra Tech Inc., 1996).

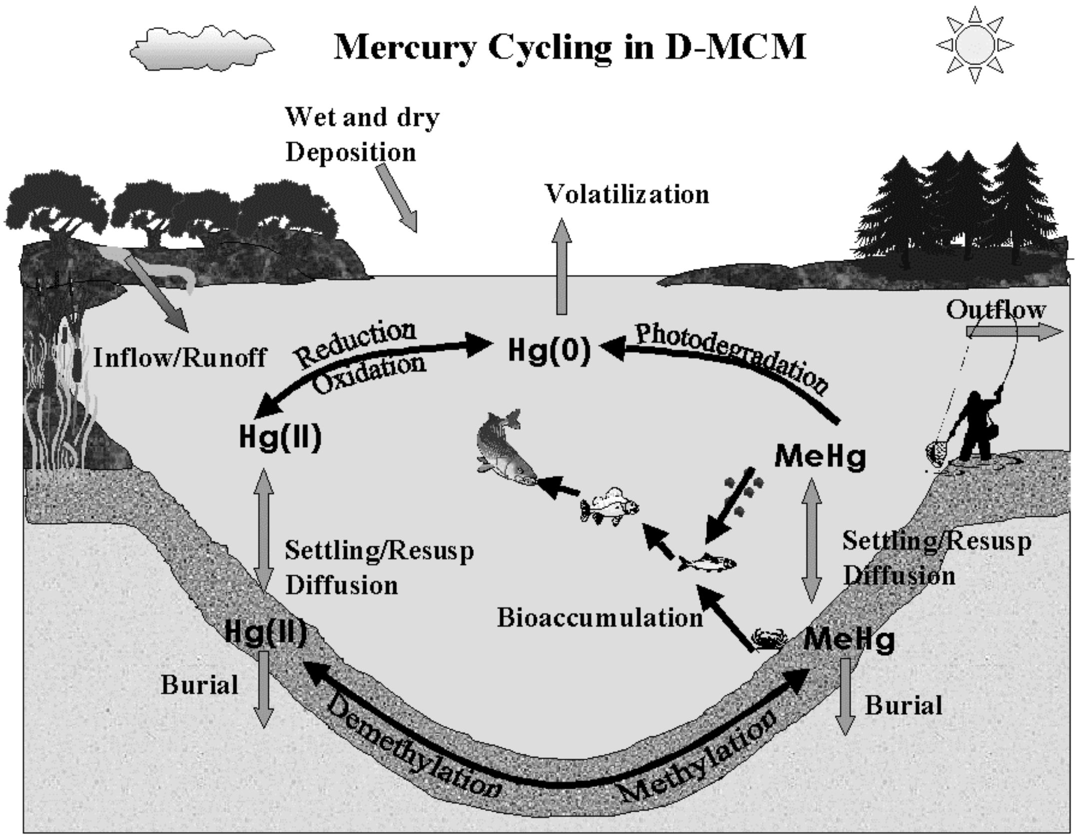


Figure 3-1
Schematic of Mercury Cycling in D-MCM

4
MODELING APPROACH

Overall the approach taken towards modeling the four lakes in this study was as follows:

- Update the calibrations for each lake on an individual basis.
- Attempt to find common values for selected model constants, that would generate reasonable results for all four study lakes.
- Carry out simulation of mercury load reductions to the four lakes, using the updated calibrations.
- Carry out simulations testing the effects of three factors on the the predicted response time of fish mercury concentrations to changes in inorganic Hg(II) loading. These factors were:
  - The fraction of sediment inorganic Hg(II) that was strongly (irreversibly) bound
  - The assumed active sediment layer thickness
  - Pelagic versus benthic-based fish diets

Further information on the approach taken for each of these tasks is provided below.

General Approach to Calibration

In general, the D-MCM calibration procedure is an iterative process involving the seven steps shown below:

1. Calibrating the particulate module (not mercury yet) to match observed or estimated bulk sedimentation rates.

2. Calibrating fish growth rate and weight versus length relationships for relevant fish species. Adjustment of population sizes to match lake productivity.

3. Adjusting, if necessary, selected model constants so that the partitioning of inorganic Hg(II) and methylmercury concentrations between dissolved and particulate phases agree with observations in both sediments and the water column.

4. Adjusting model reaction rate constants, if necessary, so that inorganic Hg(II) concentrations in water (unfiltered) and sediments (on solids) agree with observations.

5. Adjusting model reaction rate constants, if necessary, so that methylmercury concentrations in water (unfiltered) and sediments (on solids) agree with observations.

6. Adjusting model parameters, if necessary, so that methylmercury concentrations in the lower food web agree with observations.

7. Examining fish mercury concentrations. Diet and, in rare instances, species-specific bioenergetic parameters can be modified to improve agreement between the model and observed fish mercury concentrations.

Note that this exercise is based on the use of existing model equations and does not involve hypothesis testing involving different mechanisms to represent specific aspects of the mercury cycle. Such efforts are critical to the development of D-MCM and are ongoing, but were not specifically part of this study.

Various data sources for site conditions and mercury concentrations and fluxes for the four lakes were used in the calibrations.

Finding Common Calibration Values for Selected Constants

The starting points for the calibration of all four lakes were previous (unpublished) D-MCM calibrations. The particulate budgets and inorganic Hg(II) partitioning were then updated on a site-by-site basis. D-MCM does not yet have the capability to predict the binding strength of different types of particles (e.g. sand versus organic sediments). Inorganic Hg(II) and methylmercury partitioning were thus fitted to better approximate conditions expected for each site, e.g. for the primarily sandy sediments in the non-depositional littoral sediments for Lake Barco and Pallette Lake. Mercury partitioning onto the sediment particles was reduced for these sandy zones, and more of the settling organics were decomposed at the sediment interface than in previous studies. Appendix A shows model constants related to mercury partitioning for simulations assuming all mercury binding sites were readily exchangeable. Further examination of mercury partitioning in the model is needed.

An effort was made to assign values for the model constants listed in Table 4-1 that could be applied to all four lakes. Previous calibrations for the four lakes resulted in disparate estimates for these inputs. This calibration was an iterative process that basically followed the general approach outlined above with model predictions being compared to observed values concurrently for all four lakes. Simulations were carried out for 100 years or more in order to achieve near steady-state conditions. It was assumed that site data measured in the field represented long-term stable conditions, although variations with a given year would be expected. Average annual values at steady-state (e.g. after simulating for 100 years, running for one more year, saving results weekly, and determining annual averages) were compared to observed values to evaluate a particular calibration.

Table 4-1
Model Inputs Considered for Common Calibration Values

Input	Description
EfficMethylSed	Methylating efficiency of microbes, per unit of carbon decomposition and unit available inorganic Hg(II) concentration in sediments.
EfficDemethyl	Demethylating efficiency of microbes, per unit of carbon decomposition and unit available methylmercury concentration in sediments.
Ksfac	Methylmercury photodegradation rate constant at waterbody surface, per unit of surface light intensity.
KsfacReduction	Hg(II) photoreduction rate constant at waterbody surface, per unit of surface light intensity.
K_methylmercury_Benthos	Ratio of methylmercury concentrations in benthos and sediment solids.

The rate constant for methylmercury photodegradation, Ksfac, was estimated from studies of methylmercury budgets done for Lake 240 (Sellers *et al*., 1996, 2001). The rate constant for inorganic Hg(II) photoreduction (KsfacReduction) was determined from estimates of evasion of elemental mercury and from total mercury budgets from Pallette Lake and Little Rock Reference Lake (Watras *et al.,* 1994). Production of elemental mercury by photoreduction was adjusted so that when combined with that produced by methylmercury photodegradation, the total annual production of elemental mercury matched the above mentioned annual evasion estimates of elemental Hg. Once these inputs had been estimated the final inputs of interest, EfficMethylSed, EfficDemethyl and K_methylmercury_Benthos, were adjusted to obtain agreement between modeled and observed methylmercury concentrations in all four lakes. Clearly these model simulations were calibrations, not predictive applications.

Calibrations were also completed for the four lakes with different combinations of specified active sediment layer depths and fractions of readily exchangeable sediment inorganic Hg(II) (see Table 4-2). These scenarios are discussed in the following sections.

Mercury Load Reduction Scenarios

Calibrated scenarios were run for 100 years or more to achieve near steady-state conditions, with external mercury loading held constant at estimated current annual levels. The external mercury loads to the lakes (inflow, wet deposition, and dry deposition for both inorganic Hg(II) and methylmercury) were then reduced instantaneously by the same proportion to the desired levels. The predicted methylmercury concentrations in 5 year old piscivores (exactly 5 years old, immediately prior to spawning) were then followed. Simulations were run with 50% load reductions for all four lakes. Load reductions of 10 and 20 percent were also simulated for Pallette Lake.

Most of the mercury entering a lake system is inorganic Hg(II), while most of the mercury in fish is methylmercury. There are a number of steps that are required before changes in inorganic mercury loading translate into relatively steady state fish mercury concentrations. These include:

1. A change the inorganic Hg(II) load to the lake.

2. After the load changes, it takes time to change the concentration of inorganic Hg(II) in the compartment where methylation occurs.

3. Once the concentration of inorganic Hg(II) being methylated changes, methylation rates are assumed to begin to change immediately.

4. After the methylation rate changes and reaches a new steady state level, it takes additional time to change the concentration of methylmercury in compartment where methylation happens.

5. After concentrations of methylmercury in sediments and water change, it takes time for these changes to cascade up the food web to top predators.

In model simulations, the 2nd step listed above (the response of inorganic Hg(II) concentrations in the compartment where methylation happens) can be significantly affected by two assumptions:

- The depth of the active sediment layer (e.g. a few cm).
- The fraction of sediment inorganic Hg(II) on solids that is readily available to desorb rapidly and become available for methylation in porewater.

Both of these assumptions can significantly affect the size of the inorganic Hg(II) pools available for methylation that are altered in response to changes in inorganic Hg(II) supply to a lake. Changing the depth of the sediment layer will also affect step 4 above, the time required to change the concentration of methylmercury in compartment where methylation happens. It should be noted that an assumption is also needed whether to assign some or all of the porewater inorganic Hg(II) as the phase available for methylation.

Simulations were therefore performed to test the sensitivity of the model to different active sediment layer thicknesses, and different fractions of readily exchangeable mercury on sediment solids. For the purposes of this report, mercury on sediment solids that is not readily exchangeable and is slow to desorb from sediment solids is referred to as “strongly bound”.

The mercury load reduction scenarios simulated are given in Table 4-2.

Table 4-2
Load Reduction Scenarios Considered

Scenario	Load Reduction		
	10%	20%	50%
Pallette Lake - 3 cm thick sediment layer, no sediment strongly bound inorganic Hg(II)	x	x	x
Pallette Lake - 1 cm thick sediment layer, no sediment strongly bound inorganic Hg(II)			x
Pallette Lake - 3 cm thick sediment layer, 90% sediment strongly bound inorganic Hg(II)			x
Pallette Lake - 1 cm thick sediment layer, 90% sediment strongly bound inorganic Hg(II)			x
Little Rock Reference Lake – 3 cm thick sediment layer, no sediment strongly bound inorganic Hg(II)			x
Little Rock Reference Lake - 1 cm thick sediment layer, no sediment strongly bound inorganic Hg(II)			x
Lake 240 - 3 cm thick sediment layer, no sediment strongly bound inorganic Hg(II)			x
Lake 240 - 1 cm thick sediment layer, no sediment strongly bound inorganic Hg(II)			x
Lake Barco - 3 cm thick sediment layer, no sediment strongly bound inorganic Hg(II)			x
Lake Barco - 1 cm thick sediment layer, no sediment strongly bound inorganic Hg(II)			x

The Effect of the Pelagic Versus Benthic Fish Diets on Predicted Response Dynamics

When examining the relationship between inorganic Hg(II) loading to a lake and the response of fish mercury concentrations, an important aspect is the time required for changes in methylmercury concentrations in water and sediments to cascade up the food web to top predators. Since the response dynamics of methylmercury concentrations in the water column and sediments can differ, an important consideration for the response time of predatory fish mercury concentrations could be where they ultimately derive most of their methylmercury from: water or sediments. Two additional simulations were performed for Pallette Lake to examine this issue. In one simulation, benthos were effectively eliminated from the diet of all fish populations, forcing all the flow of “dietary” methylmercury to originate from the water column. For the second scenario, plankton were effectively eliminated from the diet of all fish populations, forcing all the flow of “dietary” methylmercury to originate from sediments. The predicted response dynamics for age 5 piscivores were then compared to each other and the base case calibration for Pallette Lake (3 cm active sediment layer, no strongly bound inorganic Hg(II)). In all cases, the scenario was run for 150 years following a 50% reduction in total mercury loading.

5
SITE CONDITIONS

General Characteristics

General site characteristics of the four study lakes are summarized in Table 5-1.

Lake Barco is a small acidic seepage lake in north-central Florida. It is unproductive with very low pH and DOC, but significant chloride concentrations (Schofield, 1998). Although measured concentrations of methylmercury in surface waters were low, mercury concentrations in some largemouth bass exceeded 1 ug g^{-1} wet muscle (Schofield, 1998). The hydrology and geochemistry of Lake Barco had been studied intensively previously (Pollman *et al*., 1991). The lake has a surface area of 11.4 ha with a mean depth of 3.7 m Maximum depth is slightly over 6 m. Because it is shallow, Lake Barco does not stratify consistently and remains isothermal throughout the year. Lake Barco is a flow-through seepage lake: groundwater flow enters the northern part of the lake basin, and lakewater leaks to the surficial aquifer from the southern part of the lake. The basin is undeveloped.

Pallette Lake and Little Rock Lake are in Vilas County, north-central Wisconsin. Both are seepage lakes with no surface water inflows and outflows. Hypolimnetic anoxia occurs during summer stratification (Hurley *et al.* 1994). The surrounding areas have low population densities and are remote from local municipal or industrial discharges (Watras *et al.,* 1995). Both lakes have relatively low DOC concentrations. In 1984 Little Rock Lake was partitioned (Gilmour and Riedel, 1995). One basin was acidified over a period of 6 years, while the other basin was not treated. For the purposes of this study, the untreated basin was modeled, and is referred to as Little Rock Reference Lake. Between 1988 and 1995, the Electric Power Research Institute (EPRI) and Wisconsin Department of Natural Resources (WDNR) funded two multidisciplinary studies of mercury cycling in Wisconsin seepage lakes, including Little Rock Lake and Pallette Lake. The Mercury in Temperate Lakes project (MTL) conducted from 1988-1991 studied mercury cycling in seven seepage lakes with minimal terrestrial mercury loads. The Mercury Accumulation Pathways and Processes study (MAPP) between 1992 and 1995 studied a broader set of lakes and focussed on specific processes and pathways in the mercury cycle. Many publications addressing mercury cycling in lakes emerged from these studies, including Krabbenhoft *et al.* (1998), Watras *et al.* (1995), Gilmour *et al.* (1995), Hudson *et al.* (1994), Watras *et al*. (1994), and Hurley *et al.* (1994).

Lake 240 is one of a series of lakes researched at the Experimental Lakes Area in Ontario. It is an oligotrophic drainage lake with an area of 44.1 ha and a mean depth of 6.1 m (Sellers *et al*., 2001).

Table 5-1
Site Characteristics of the Four Lakes

Characteristic	Units	Lake 240	Little Rock Reference Lake	Pallette Lake	Lake Barco
Lake Area	ha	44	81	70	11.8
Mean surface water depth	m	6.0	3.1	9.6	3.7
Water Temperatures (monthly means)	C	2 - 21	2 - 23	2 - 23	12 - 30
Precipitation	mm	703	770	770	1348
Principal flow pattern		Surface flow	Seepage	Seepage	Seepage
Stratification		yes	yes	yes	intermittent
Hypolimnetic Anoxia		no	yes	yes	no
Dissolved Organic Carbon	mg L^{-1}	7	3	5	0.85
Surface water pH		6.9	6.0	7.2	4.5
Surface water chloride	mg L^{-1}	0.4	0.3	0.3	5.0
Surface water sulfate	μeq L^{-1}	26	52	52	150
Sedimentation (littoral)	mm yr^{-1}	~ 0	~ 0.2	~ 0	~ 0
Sedimentation (profundal)	mm yr^{-1}	1.1	1	0.6	1.2
Settling solids	mg L^{-1}	~ 0.9	~ 0.7	~1.0	~0.8
Predatory fish		Northern pike			Largemouth bass

Mercury Loading Rates to the Lakes

Estimated Atmospheric Mercury Deposition Rates

Precipitation data and mercury deposition data were compiled from various sources to estimate wet mercury deposition for the four lakes. Wisconsin precipitation and mercury deposition data for Trout Lake, WI for the years 1996 through 1999 (MDN data) were used to construct atmospheric wet deposition loads for Little Rock and Pallette Lakes. Average monthly precipitation and wet mercury deposition rates were calculated for the five years of data. These numbers were summed to obtain an average annual precipitation and wet Hg deposition for Trout Lake and the volume weighted mean concentration was then calculated from these annual values. The reported deposition data was given as total mercury and was assumed to be inorganic Hg(II) in this analysis. The resulting annual wet deposition rates estimated for Little Rock Reference Lake and Pallette Lake were 8.1 ug m^{-2} yr^{-1}. Dry deposition of inorganic Hg(II) was assumed to be constant throughout the year at an annual rate of 4.05 ug m^{-2} yr^{-1} (assumed 50% of the annual wet deposition).

A value of 7 ug m^{-2} yr^{-1} was used for the estimate of mean annual wet deposition rate for inorganic Hg(II) to Lake 240 (St. Louis *et al.,* 2001). Dry deposition of inorganic Hg(II) directly to the surface of Lake 240 was assumed to be less than 1 ug m^{-2} yr^{-1}.

Wet mercury deposition and dry deposition estimates for Lake Barco were taken from a previous study of Lake Barco (Harris *et al*., in preparation).

Wet mercury deposition for Little Rock, Pallette and Lake 240 was adjusted so that there was no atmospheric mercury loading during periods of the simulations when the lake had ice cover. Mercury deposition during this period was "stored" and later applied to the lake during the month following ice breakup.

Estimates of Mercury Loads in Inflows

Of the four lakes modeled, surface water inflow was significant only for Lake 240. Surface and groundwater inflows were assumed not to represent significant sources of mercury in the other lakes. Data for monthly surface flows into Lake 240 from the Lake 239 outflow and Lake 470 outflow were averaged from1969 through 1997 to provide mean monthly stream inflow values for the Lake 240 simulation. Direct runoff to Lake 240 was also included, based on an estimated terrestrial water runoff value of 0.226 m $year^{-1}$(K. Beaty unpublished data). This value was based on a water budget from a nearby similar catchment (Lake 239 NW sub-basin). A methylmercury concentration of 0.11 ng L^{-1} was used for the overall Lake 240 inflow on the basis of inflow concentrations estimated for three surface flows (L239 outflow, L470 outflow, direct runoff) by Sellers *et al*. (2001), combined with the long-term flows discussed above. Note that the flow data are long-term averages while the estimates for mercury concentrations to Lake 240 are based on data for one year period (March 1995 to March 1996) from Sellers *et al*. (2001). Inflow concentrations of inorganic Hg(II) to Lake 240 were estimated to be 3.1 ng L^{-1}.

6
RESULTS

Calibration Results

Estimated Values for Selected Model Constants

Estimates obtained for model constants considered for common calibration values are given in Table 6-1. Reasonable agreement was obtained between model predictions and observed data for methylmercury and total mercury concentrations for all four lakes (see Table 6-2 through Table 6-9) when consistent input values were used for the parameters in Table 6-1, with the exception of the photoreduction coefficient (KsfacReduction) for Lake Barco. The value of KsfacReduction estimated from data for Little Rock Reference Lake and Pallette Lake produced unrealistically high inorganic Hg(II) reduction rates in Lake Barco. This led to predicted inorganic Hg(II) and methylmercury concentrations in the lake system being significantly lower than those observed. The value of KsfacReduction was therefore reduced by three orders of magnitude as shown in Table 6-1 to achieve better results. It should also be reinforced that model constants related to mercury partitioning onto solids had to be adjusted between sites (Appendix A).

Table 6-1
Estimated Values for Selected Model Constants

Model Constant	Units	Lake 240	Little Rock Reference Lake	Pallette Lake	Lake Barco
EfficMethylSed	g methylmercury g^{-1} TOC labile	0.0176	0.0176	0.0176	0.0176
EfficDemethyl	g ElemHg g^{-1} TOC labile	0.02	0.02	0.02	0.02
Ksfac	ug methylmercury m^{-3} day^{-1}	0.00088	0.00088	0.00088	0.00088
KsfacReduction	ug Hg(II) m^{-3} day^{-1}	0.0027	0.0027	0.0027	0.0000027
k_methylmercury_ Benthos	(ug methylmercury g^{-1} wet benthos) per (ug methylmercury g^{-1} sed)	40	40	40	40
Note: Descriptions of these constants are provided in Table 4-1.					

Calibrated Inorganic Hg(II) Concentrations

Simulated and observed inorganic Hg(II) concentrations for the calibrations using the assumptions of a 3 cm active sediment layer and no strongly bound mercury are presented in Table 6-2 through Table 6-5 for the four lakes. The model results for these tables are all mean annual values based on weekly model outputs. Figure 6-1 shows mean values for observations and calibrated inorganic Hg(II) concentrations for surface waters. Figure 6-2 and Figure 6-3 show observations and calibrated inorganic Hg(II) concentrations for littoral and profundal sediments respectively in the four study lakes. The sediment figures show mean annual predicted values, as well as the corresponding maximum and minimum observed values.

Table 6-2
Simulated and Observed Inorganic Hg(II) Concentrations for Pallette Lake

Compartment/Phase	Units	D-MCM with 3cm sediment layer, no strongly bound Hg	Observed	Notes on observations	Reference
Epilimnion (unfiltered)	ng L^{-1}	0.65	0.47	Observed is mean value for samples from 1990 –1994	Watras *et al.* (1998)
Sediment solids (littoral)	ng g^{-1}dry	4	0.3 - 2.7	Observations from depths <9m	Watras *et al.* (1998); C. Watras (unpublished data)
Sediment solids (profundal)	ng g^{-1}dry	73	71 - 156	Observations from depths >13 m	Watras *et al.* (1998); C. Watras (unpublished data)

Table 6-3
Simulated and Observed Inorganic Hg(II) Concentrations for Little Rock Reference Lake

Compartment/Phase	Units	D-MCM with 3cm sediment layer, no strongly bound Hg	Observed	Notes on observations	Reference
Epilimnion (unfiltered)	ng L^{-1}	1.04	0.85	Observed is mean value for samples from 1990 –1994	Watras *et al.* (1998)
Sediment solids	ng g^{-1}dry	122 (littoral) 99(profundal)	76-191	Observations include samples in littoral and profundal zones	Watras *et al.* (1998); Gilmour and Riedel (1995)

Table 6-4
Simulated and Observed Inorganic Hg(II) Concentrations for Lake 240

Compartment/Phase	Units	D-MCM with 3cm sediment layer, no strongly bound Hg	Observed	Notes on observations	Reference
Epilimnion (unfiltered)	ng L^{-1}	1.49	0.9 – 1.81 (Mean 1.38)	Observations represent range for surface samples collected between May 2000 and September 2001	K. Sandilands (unpublished data)
Sediment solids (littoral / profundal)	ng g^{-1} dry	3.3 (littoral) 94.0 (profundal)	3.2 (Littoral)	Observation is littoral sample from <1 m depth	C. Gilmour (unpublished data)

Table 6-5
Simulated and Observed Inorganic Hg(II) Concentrations for Lake Barco

Compartment/Phase	Units	D-MCM with 3cm sediment layer, no strongly bound Hg	Observed	Notes on observed values	Reference
Epilimnion (unfiltered)	ng L^{-1}	1.4	1.03	Observed value is mean of 101 samples taken from 4 littoral and pelagic stations, including replicates and different depths. Sample dates from 10/95 thru 3/97	Harris *et al.* (in preparation)
Zooplankton	ng g^{-1} dry	46 - 80	49 – 303	Observed values are means of HgT concentrations for 4 sampling dates	Sigler (1998)
Sediment solids (littoral)	ng g^{-1} dry	46	30 – 331	Observed values are HgT concentrations	Sigler (1998)
Sediment solids (profundal)	ng g^{-1} dry	111	152 – 186	Observed values are HgT concentrations	Sigler (1998)

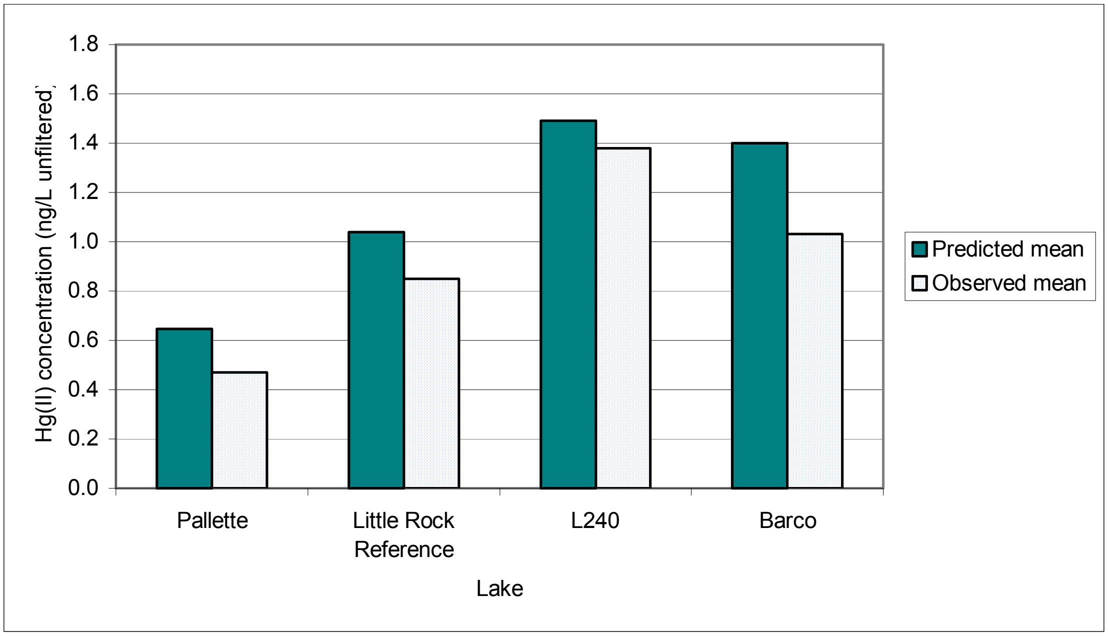


Figure 6-1
Calibrated and Observed Inorganic Hg(II) Concentrations in Surface Waters for the Study Lakes

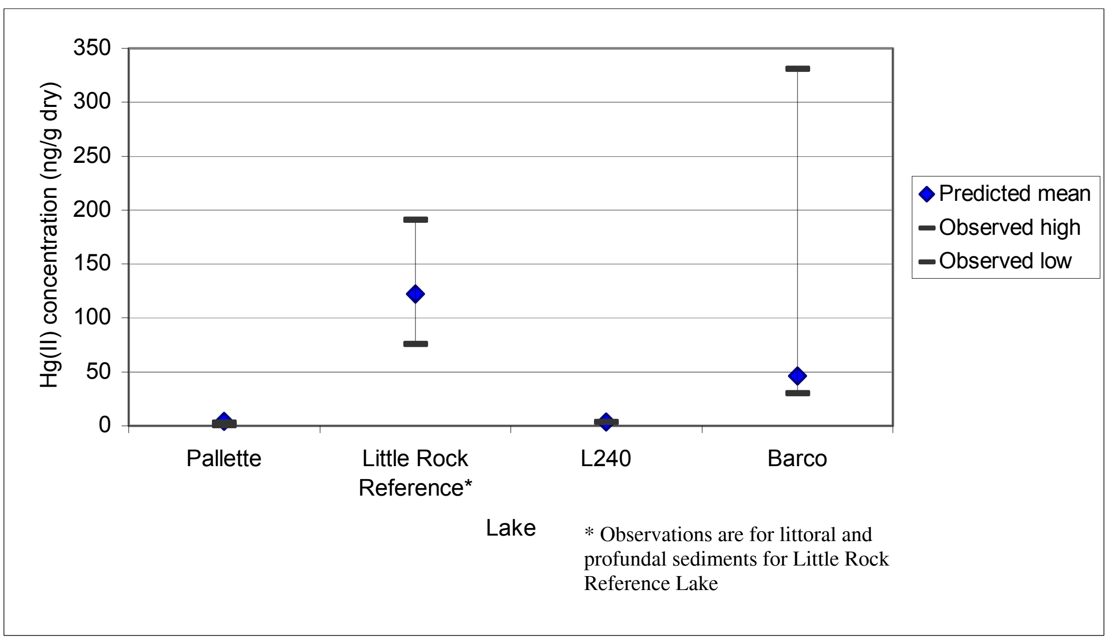


Figure 6-2
Calibrated and Observed Inorganic Hg(II) Concentrations in Littoral Sediments for the Study Lakes

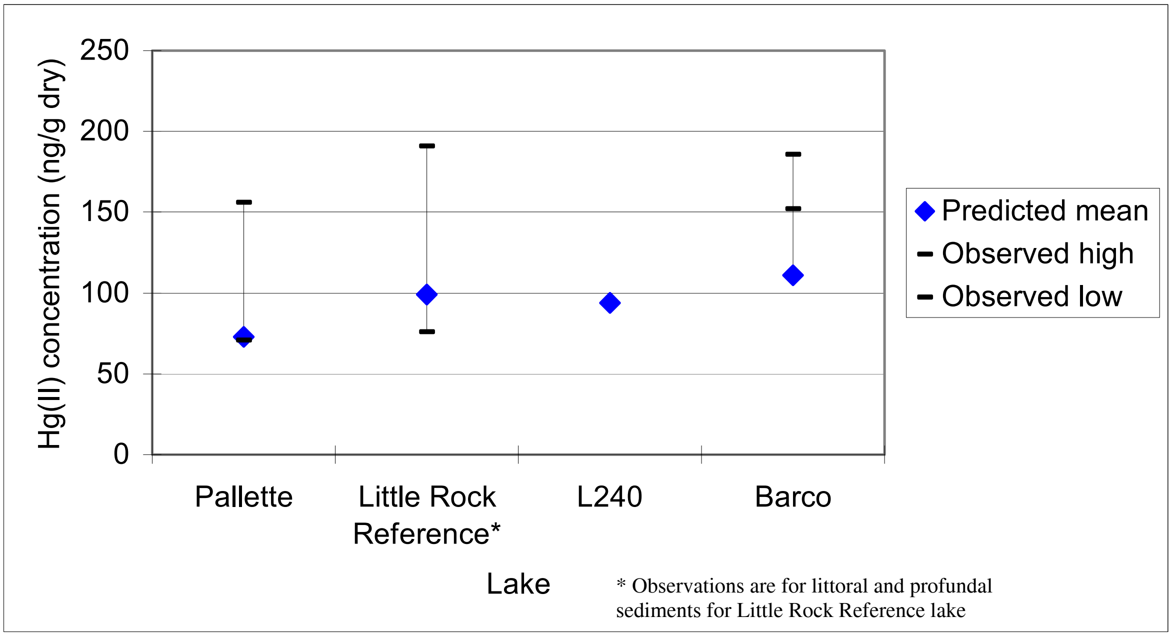


Figure 6-3
Calibrated and Observed Inorganic Hg(II) Concentrations in Profundal Sediments for the Study Lakes

Predicted Methylmercury Concentrations

Simulated and observed methylmercury concentrations for the calibrations using the assumptions of a 3 cm active sediment layer and no strongly bound mercury are presented in Table 6-6 through Table 6-9 for the four study lakes. Model results are mean annual values based on weekly model outputs. Figure 6-4 shows mean values for observations and calibrated methylmercury concentrations in surface waters. Figure 6-5 and Figure 6-6 show observations and calibrated methylmercury concentrations in sediments for the four study lakes. The sediment figures show mean annual predicted methylmercury concentrations, as well as the corresponding maximum and minimum observed values.

Table 6-6
Simulated and Observed Methylmercury Concentrations for Pallette Lake

Compartment/Phase	Units	D-MCM with 3cm sediment layer, no strongly bound Hg	Observed	Notes on observed values	Reference
Epilimnion (unfiltered)	ng L^{-1}	0.12	0.05	Observed is mean value for samples from 1990 –1994	Watras *et al.* (1998)
Sediment solids (littoral)	ng g^{-1} dry	0.11	0.06 - 0.07	Observations from depths <9m	Watras *et al.* (1998); C. Watras (unpublished data)
Sediment solids (profundal)	ng g^{-1} dry	1.73	0.16 - 1.91	Observations from depths >13 m	Watras *et al.* (1998); C. Watras (unpublished data)
Yellow perch (age 3)	ug g^{-1} (whole body)	0.05	0.034	Observation is mean value for 10 fish	C. Watras (unpublished data)

Table 6-7
Simulated and Observed Methylmercury Concentrations for Little Rock Reference Lake

Compartment/Phase	Units	D-MCM with 3cm sediment layer, no strongly bound Hg	Observed	Notes on observations	Reference
Epilimnion (unfiltered)	ng L^{-1}	0.05	0.07	Observed is mean value for samples from 1990 –1994	Watras *et al.* (1998)
Sediment solids	ng g^{-1} dry	1.2 (littoral) 1.0 (profundal)	0.5 – 4.6	Observations include samples in littoral and profundal zones	Watras *et al.* (1998); Gilmour and Riedel (1995); C. Watras (unpublished data)
Yellow perch (age 1)	ug g^{-1} (whole body)	0.05	0.074	Observation is mean value for 15 fish	C. Watras (unpublished data)
Yellow perch (age 3)	ug g^{-1} (whole body)	0.09	0.14	Observation is mean value for 4 fish	C. Watras (unpublished data)

Table 6-8
Simulated and Observed Methylmercury Concentrations for Lake 240

Compartment	Units	D-MCM with 3cm sediment layer, no strongly bound Hg	Observed	Notes on observed values	Reference
Epilimnion (unfiltered)	ng L^{-1}	0.12	0.079	Value is average of 22 surface samples between May 2000 and September 2001	K. Sandilands (unpublished data)
Zooplankton	ng g^{-1} dry	68	35 -178		M. Paterson (unpublished data)
Benthos/ macroinvertebrates (littoral)	ng g^{-1} wet	49 (littoral) 27(profundal)	0.2 - 87	Observations are converted from dry to wet weight estimates assuming 85% water content	C. Podemski (unpublished data) *
Sediment solids (littoral/profundal)	ng g^{-1} dry	1.2 (littoral) 0.7 (profundal)	0.3 (littoral)	Sample for depth less than 1 m	C. Gilmour (unpublished data)
Yellow perch (young of year)	ug g^{-1} (wet muscle)	0.06**	0.072 (2000) 0.105 (2001) 0.094 (2002)	Observations are means for each year noted	P. Blanchfield (unpublished data)

Notes:
* Observed values converted to wet basis assuming 85% water.
** Predicted for September

Table 6-9
Simulated and Observed Methylmercury Concentrations for Lake Barco

Compartment	Units	D-MCM with 3cm sediment layer, no strongly bound Hg	Observed	Notes on observations	Reference
Epilimnion (unfiltered)	ng L^{-1}	0.01	0.018	Observed value is mean of 101 samples taken from 4 littoral and pelagic stations, including replicates and different depths. Sample dates from 10/95 thru 3/97	Harris *et al.* (in preparation)
Zooplankton	ng g^{-1} dry	30	74	Observation is mean of 4 samples, March 1997	Morrison and Watras (1997)
Benthos/littoral macroinvertebrates	ng g^{-1} wet	12	26	Observation is mean value for four samples. Organisms were odonates. Concentrations are converted from dry weight basis assuming they are 80% water.	Morrison and Watras (1997)
Sediment solids (littoral)	ng g^{-1} dry	0.3	0.02 – 0.38	Observations are from surface grabs at 4 sites.	Sigler (1998)
Sediment solids (profundal)	ng g^{-1} dry	1.7	1.9 – 6.9	Observations are range for 0.5 cm slices in upper 3 cm	Sigler (1998)
Mosquitofish (0.5 yrs)	ug g^{-1} wet whole body	0.1	0.085	Mosquitofish observation is overall mean of means from 4 sampling dates, total n= 78 Concentrations are converted from dry to wet weight basis assuming fish are 75% water.	Morrison and Watras (1997)
Largemouth Bass (2 yrs)	ug/g wet muscle	0.36	0.54	Mean value, n=17	Schofield (1998)

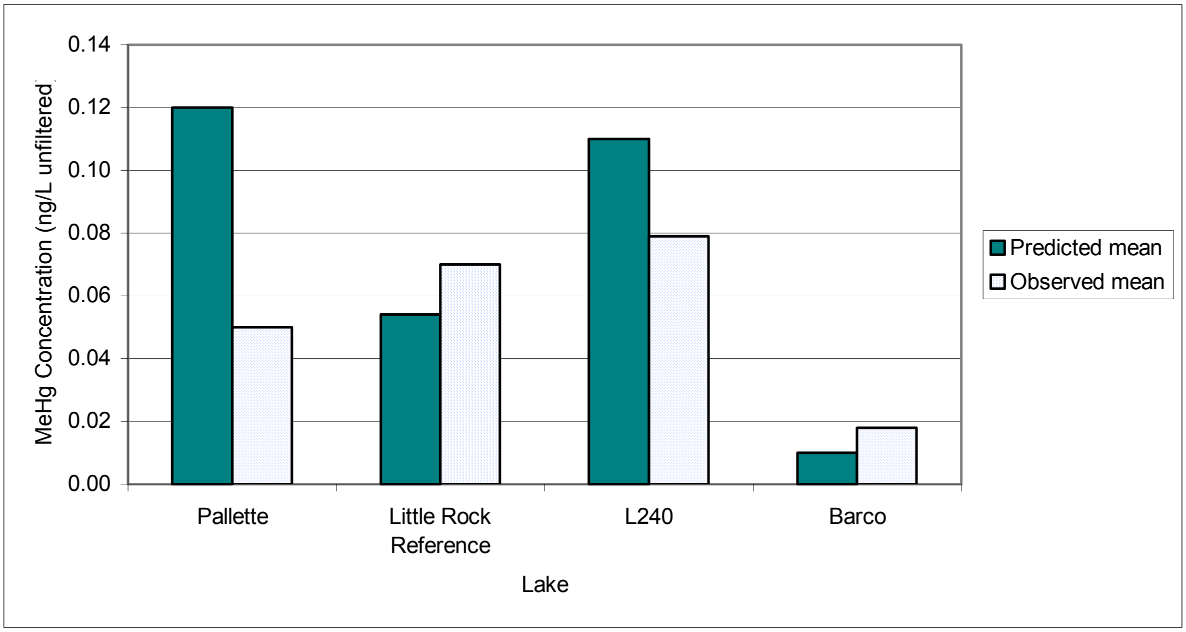
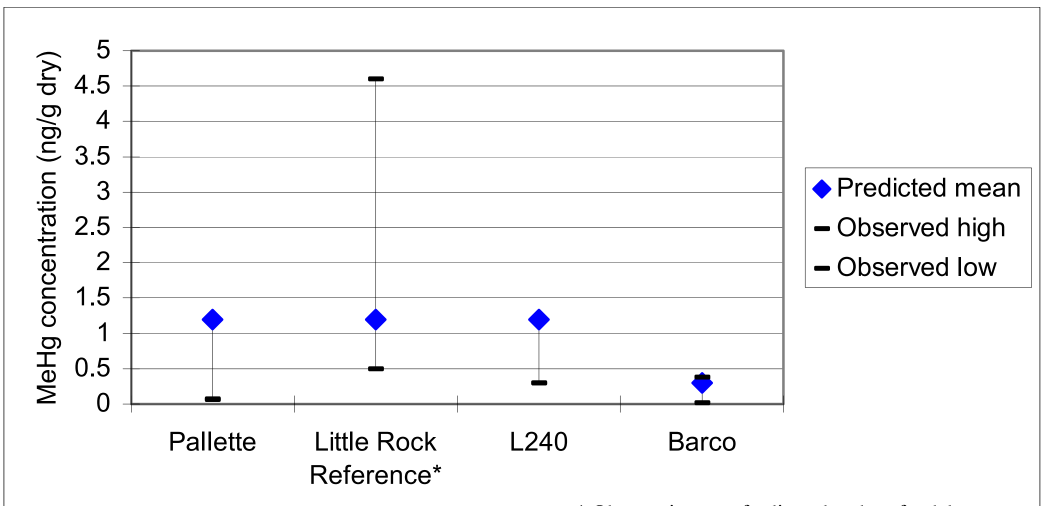


Figure 6-4
Calibrated and Observed Methylmercury Concentrations in Surface Waters for the Study Lakes



* Observations are for littoral and profundal sediments for Little Rock Reference Lake

Figure 6-5
Calibrated and Observed Methylmercury Concentrations in Littoral Sediments for the Study Lakes

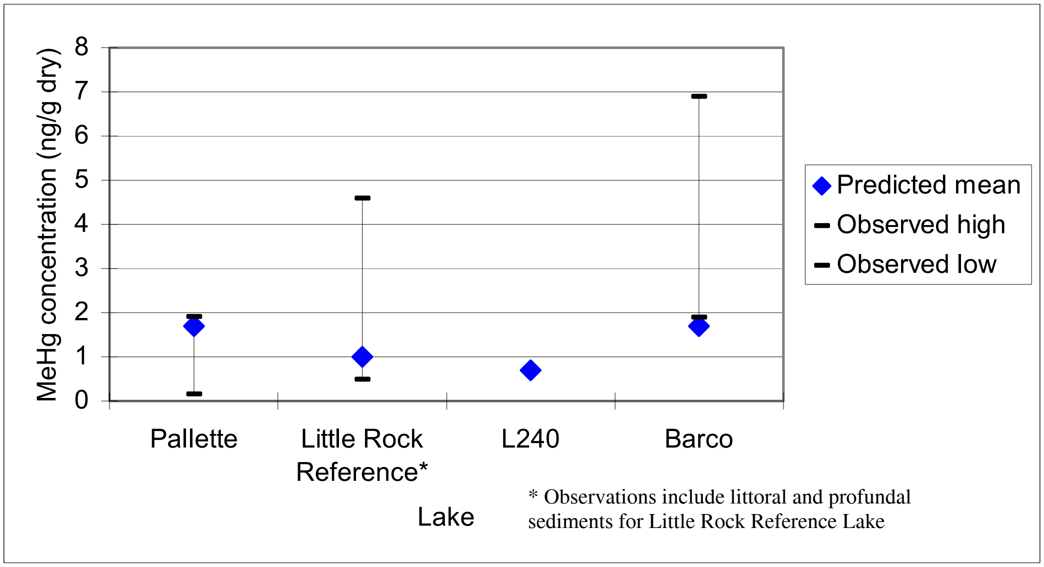


Figure 6-6
Calibrated and Observed Methylmercury Concentrations in Profundal Sediments for the Study Lakes

Predicted Annual Mercury Fluxes

Estimated sources of inorganic Hg(II) for the four study lakes are shown in Figure 6-7 as mean annual fluxes on a whole-lake basis. Model predictions for inorganic Hg(II) losses for the four lakes are presented in Figure 6-8 and Figure 6-9. Figure 6-8 gives absolute annual losses in ug m^{-2} yr^{-1} on a whole lake basis while Figure 6-9 presents annual predicted losses as a fraction of total losses.

Direct atmospheric deposition, both wet and dry, dominated the estimated inorganic Hg(II) loading to Pallette Lake, Little Rock Reference Lake and Lake Barco, while the largest estimated source of inorganic Hg(II) to Lake 240 was inflow from the watershed (Figure 6-7).

The relative importance of different predicted removal mechanisms for inorganic Hg(II) for the four lakes varied between lakes(Figure 6-8 and Figure 6-9). Burial of inorganic Hg(II) (below 3cm) was significant for all four lakes, ranging from 43 to 95 percent of the predicted inorganic Hg(II) removal rates. Outflow was only significant for the drainage lake (Lake 240), representing 40 percent of predicted inorganic Hg(II) removal. It should be noted that the outflow reported here includes surface and seepage fluxes. Surface flow accounted for 83 percent of the predicted annual total outflow of inorganic Hg(II) in Lake 240 however. The importance of inorganic Hg(II) photoreduction was predicted to vary across the four lakes, ranging from 2 to 43 percent of the overall lake system Hg(II) losses.

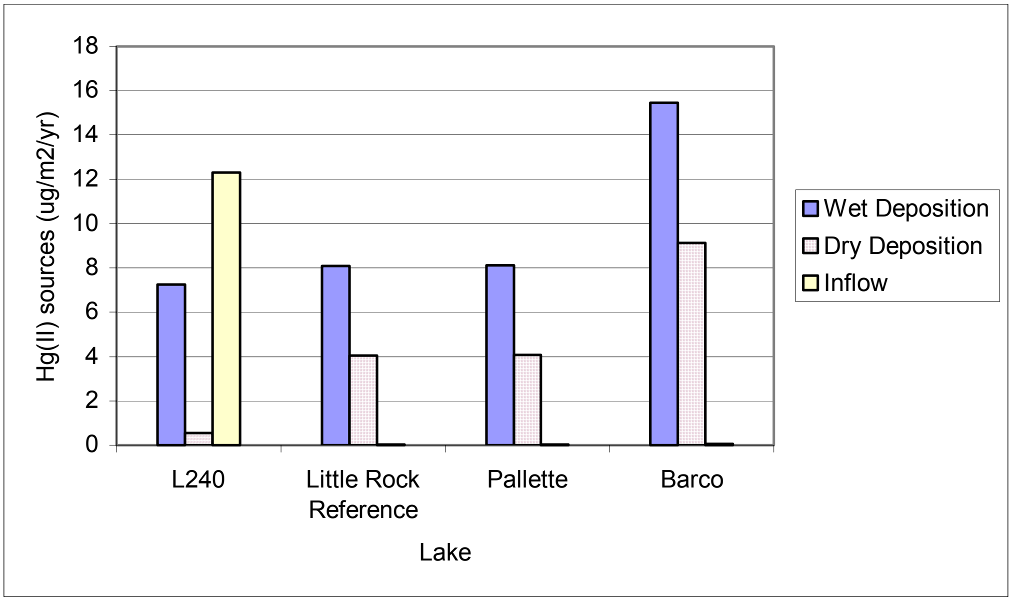


Figure 6-7
Estimated Inorganic Hg(II) Sources to the Study Lakes (whole-lake basis)

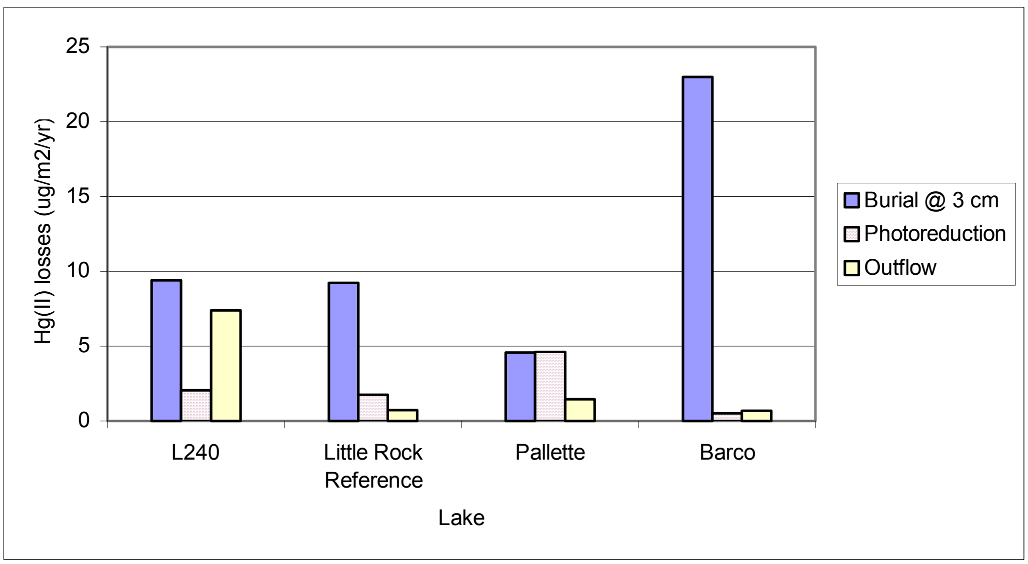


Figure 6-8
Predicted Annual Inorganic Hg(II) Losses for the Study Lakes (whole-lake basis)

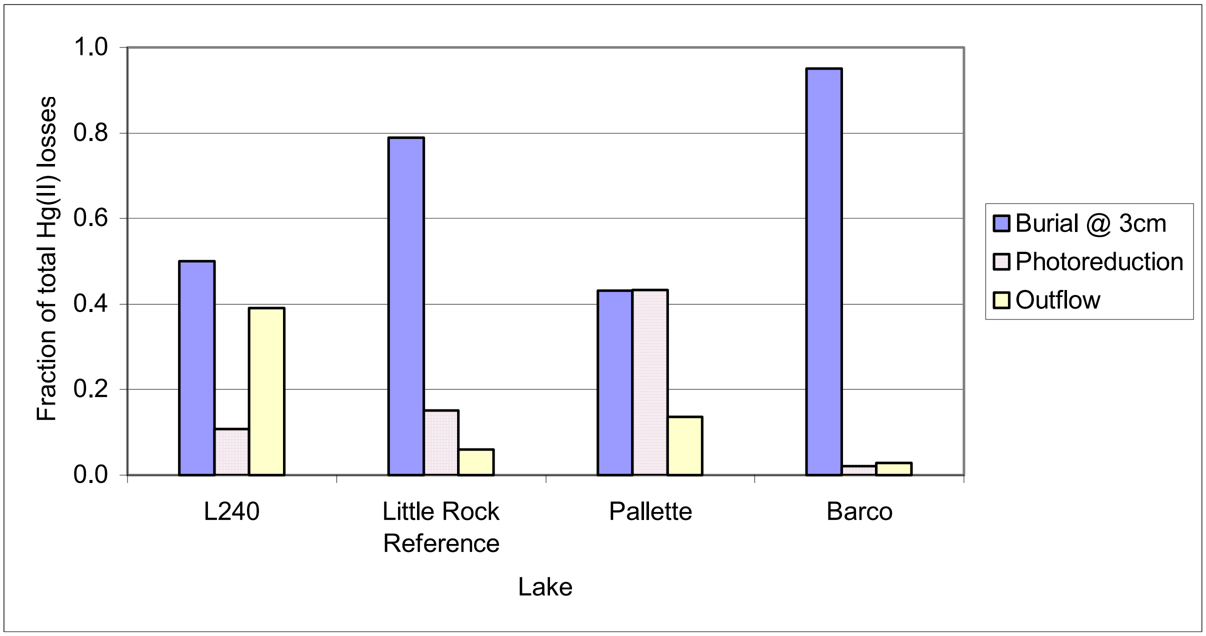


Figure 6-9
Predicted Annual Inorganic Hg(II) Losses as a Fraction of Overall Inorganic Hg(II) Losses for the Study Lakes

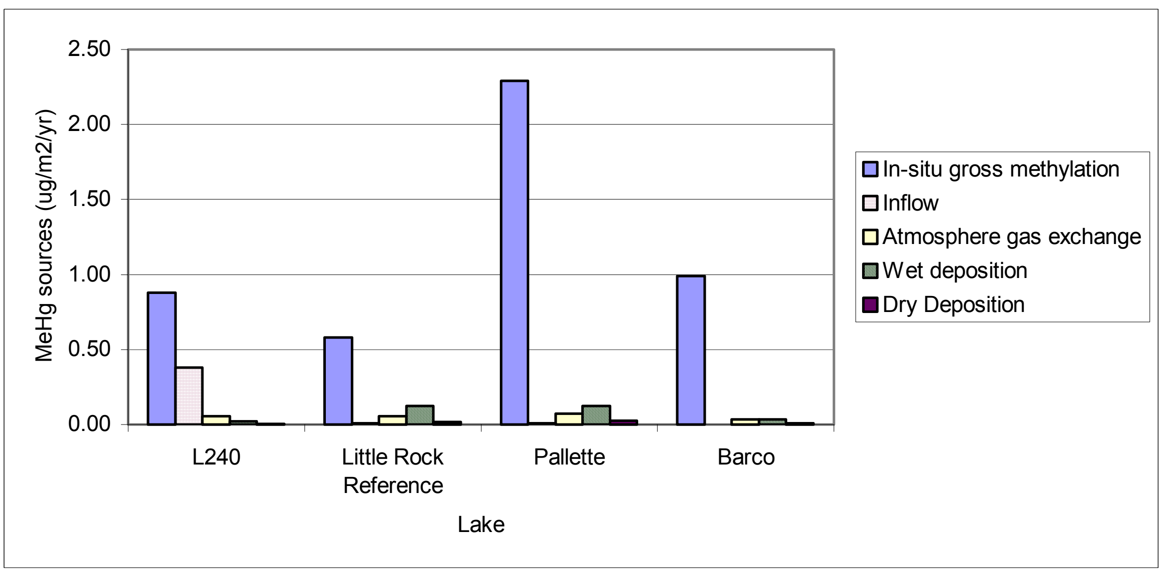


Figure 6-10
Estimated Annual Methylmercury Sources for the Study Lakes (whole-lake basis)

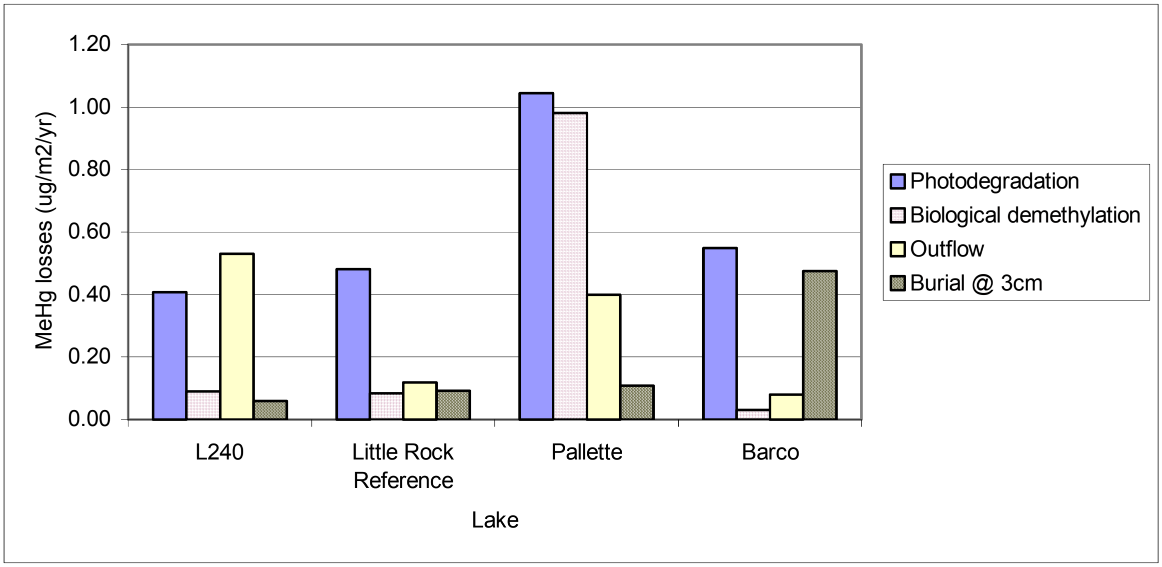


Figure 6-11
Predicted Annual Methylmercury Losses for the Study Lakes (whole-lake basis)

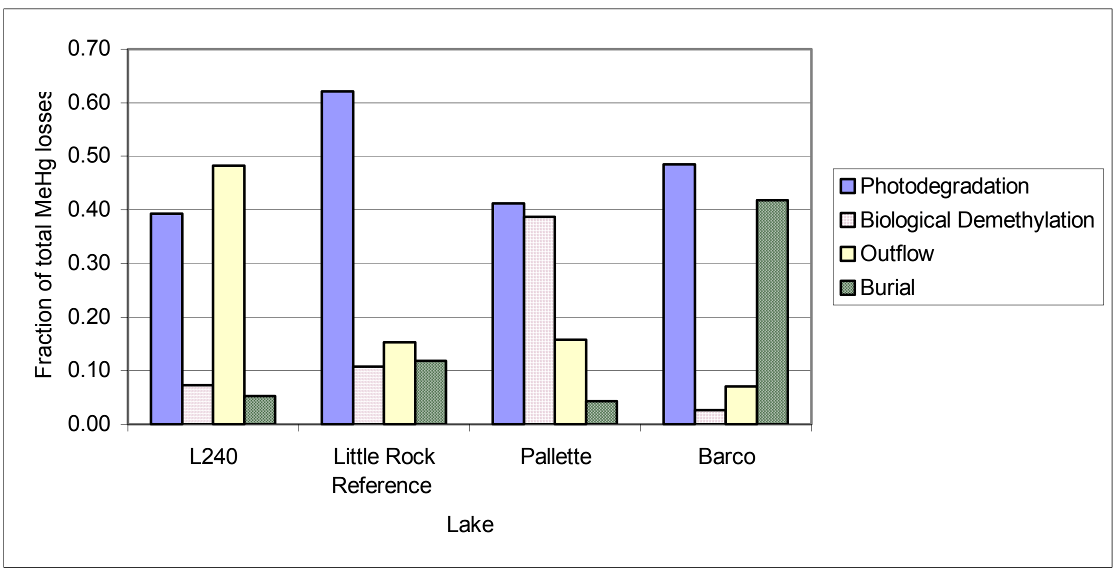


Figure 6-12
Predicted Annual Methylmercury Losses as a Fraction of Overall Methylmercury Losses for the Study Lakes (whole-lake basis)

Estimated and predicted methylmercury sources are shown as mean annual fluxes in Figure 6-10 for the four lakes. In all four lakes, in-situ methylation (gross or net) was the dominant calibrated source of methylmercury (Figure 6-10).

Annual predicted methylmercury losses expressed on a ug m^{-2} yr^{-1} basis are charted in Figure 6-11. Predicted methylmercury losses expressed as a fraction of the total methylmercury losses given in Figure 6-12. Photodegradation was predicted to be an important mechanism for all four lakes. This is partly a result of the assumption that gross methylation and gross biological demethylation rates occur at magnitudes comparable to the estimated net methylation rates. It is quite possible that the same net methylation could occur with higher individual rates of gross methylation and demethylation, in which case the relative importance of photodegradation of methylmercury as a system loss pathway would be reduced. The importance of other removal mechanisms varied from lake to lake. Outflow of methylmercury contributed significantly to total predicted methylmercury removal only for Lake 240 (the other lakes were seepage lakes). Burial was only predicted to be a primary removal pathway for methylmercury in Lake Barco (Figure 6-12).

Mercury Load Reduction Scenarios

50% Load Reductions

Plots of the simulated responses of methylmercury concentrations in five year old piscivores to an instantaneous reduction of 50% in mercury loading in the four lakes are presented in Figure 6-13 through Figure 6-16. All external mercury loads of inorganic Hg(II) and methylmercury were reduced by 50% at the same time as a step function, including wet deposition, dry deposition and inflow of both methylmercury and inorganic Hg(II). For all the modeled sites, the base case simulations assumed a 3 cm active sediment layer with all inorganic Hg(II) in the sediments considered to be freely exchangeable (no strongly bound inorganic Hg(II) on the sediment solids).

The “proportional” values referred to in Figure 6-13 through Figure 6-18 are the long term steady state concentrations in the fish that would be expected if their long term response was proportional to the loading changes.

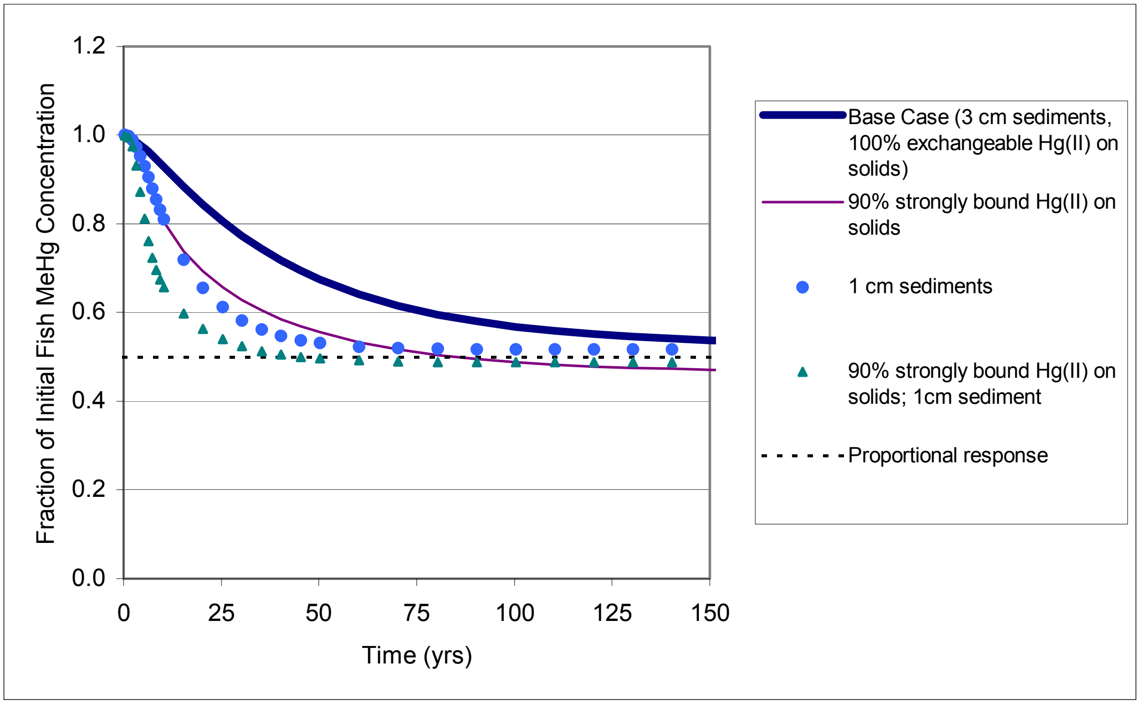


Figure 6-13
Simulated Methylmercury Responses in Age 5 Piscivores in Pallette Lake - 50% Load Reduction

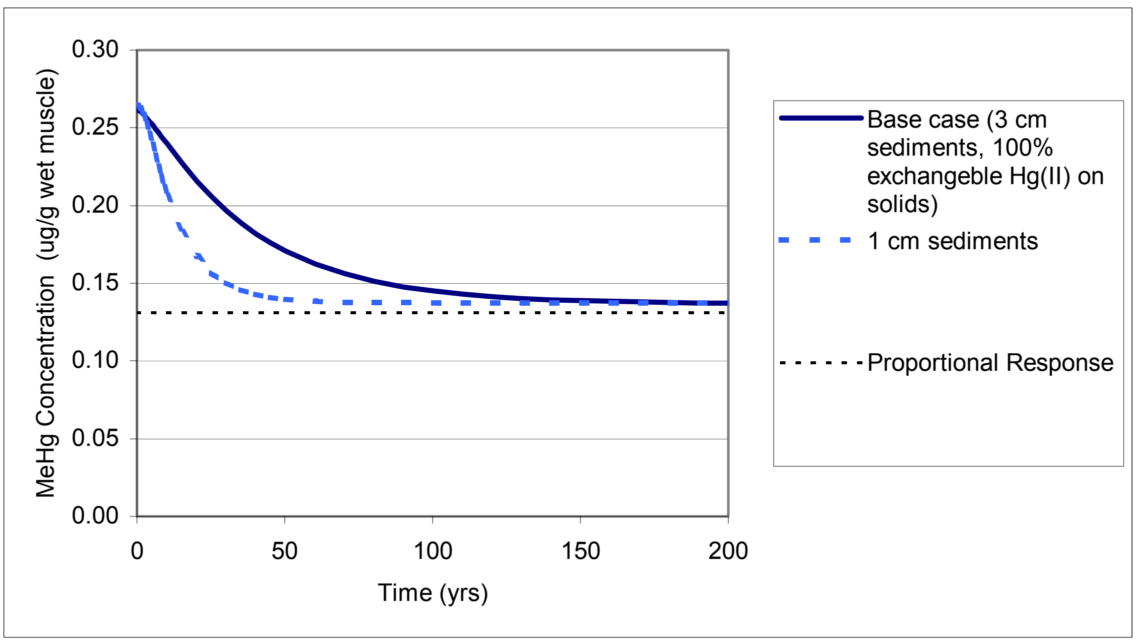


Figure 6-14
Simulated Methylmercury in Age 5 Piscivores in Little Rock Reference Lake - 50% Load Reduction

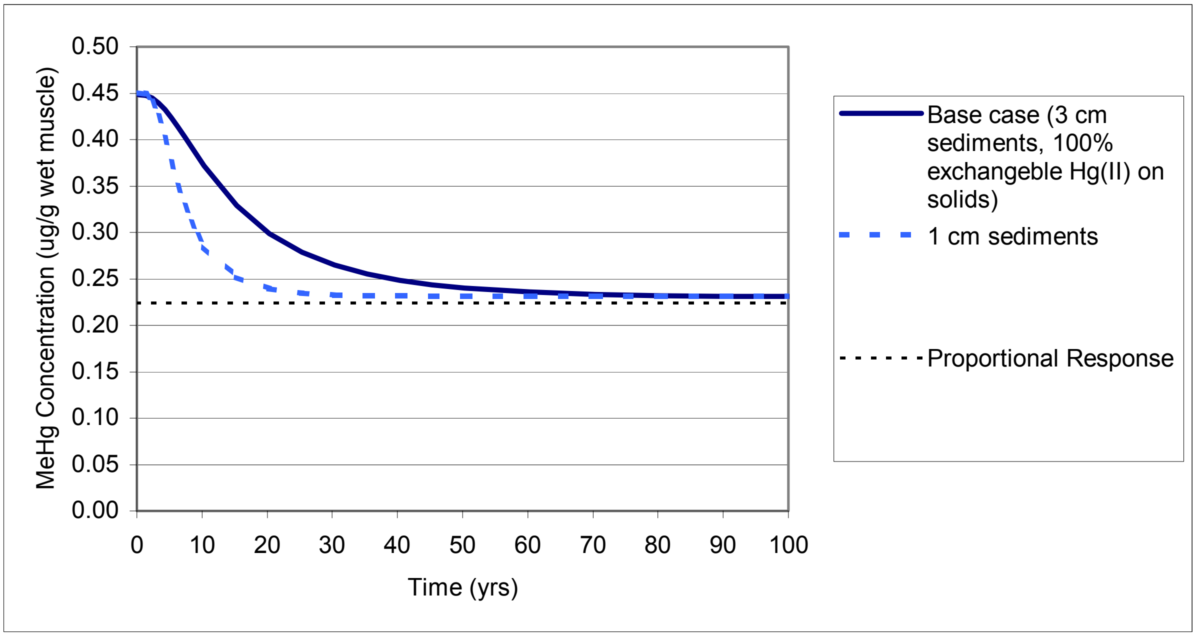


Figure 6-15
Simulated Methylmercury Response in Age 5 Piscivores in Lake 240 - 50% Load Reduction

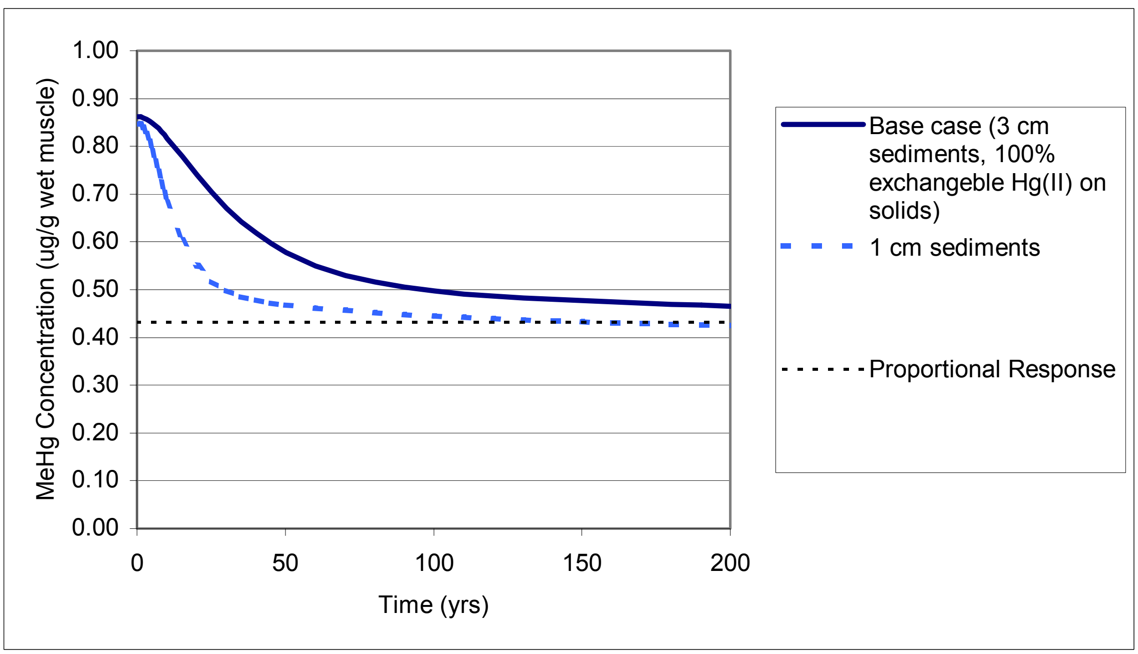


Figure 6-16
Simulated Methylmercury Response in Age 5 Piscivores in Lake Barco - 50% Load Reduction

The predicted responses of 5 year old piscivores in the four lakes to 50% load reductions tended to follow an exponential decline after an initial brief lag, for simulations with all mercury binding on solids being readily exchangeable. It should be noted that some situations modeled did not exhibit a simple exponential response for fish, as discussed in later sections. The assumption of a thinner active sediment layer (1 cm) significantly reduced the predicted response times for all sites. The inclusion of strongly bound inorganic Hg(II) in sediments also accelerated the predicted response of fish mercury concentrations for Pallette Lake (the only lake where the effects of strongly bound mercury were tested).

The response half-lives were estimated as the time required for half of the final change in concentration to occur, where the final concentration was assumed to be a proportional 50% reduction. In other words, the half-life was the time required to achieve a 25% reduction in concentration. Calculated half-lives for the dynamic responses for 5 year old piscivore methylmercury are provided in Table 6-10 for simulations with all solid phase binding sites being readily exchangeable. Table 6-11 shows the same results, but expressed as the time predicted for the fish to achieve 90% of the long term steady state concentration.

Table 6-10
Estimated Half-Lives for the Predicted Response of Methylmercury Concentrations 5 Year Old Piscivores – Simulations with 100% Exchangeable Inorganic Hg(II)

	Estimated Half-life (years)	
Lake	**1 cm sediment layer**	**3 cm sediment layer**
Pallette Lake	13.6	34.2
Little Rock Reference Lake	12.1	30.0
Lake 240	6.9	14.5
Lake Barco	13.2	34.5

Table 6-11
Predicted Time to Achieve 90% of New Steady State for age 5 Piscivores for Scenarios with all Inorganic Hg(II) Readily Exchangeable

	Years to Achieve 90% of the Long-Term Response	
Lake	**1 cm**	**3 cm**
Pallette Lake	39	122
Little Rock Reference Lake	36	107
Lake 240	17	42
Lake Barco	54	160

Table 6-12 shows the times predicted for 90% of the final response to occur in 5 year old piscivores in Pallette Lake for various scenarios, assuming the response was ultimately proportional to the reduction in inorganic Hg(II) loading. Included in this table are results for scenarios with strongly bound Hg(II) on solids. Clearly assumptions regarding the thickness of the sediment layer and strongly bound Hg(II) can significantly affect model predictions about response times.

Table 6-12. Predicted Time to achieve 90% response in 5 yr old piscivores in Pallette Lake following a 50% load reduction

Scenario	90% response (years)	Half-life (years)
3 cm sed layer, no strongly bound inorganic Hg(II)	122	34
3 cm sed layer, 90% strongly bound inorganic Hg(II)	53	14
1 cm sed layer, no strongly bound inorganic Hg(II)	39	13.6
1 cm sed layer, 90% strongly bound inorganic Hg(II)	23	6.6

The predicted responses of inorganic Hg(II) and methylmercury concentrations in different compartments in Pallette Lake are compared in Figure 6-17 under based case conditions with a 3 cm active sediment layer and 100% exchangeable Hg(II) in sediments. The response dynamics are similar in all cases, with fish mercury concentrations responding slightly slower than methylmercury in other compartments. Methylmercury concentrations in littoral sediments in turn slightly lagged inorganic Hg(II) concentrations in the same compartment. This was likely partly due to the time required for methylmercury concentrations to respond once methylation rates changed.

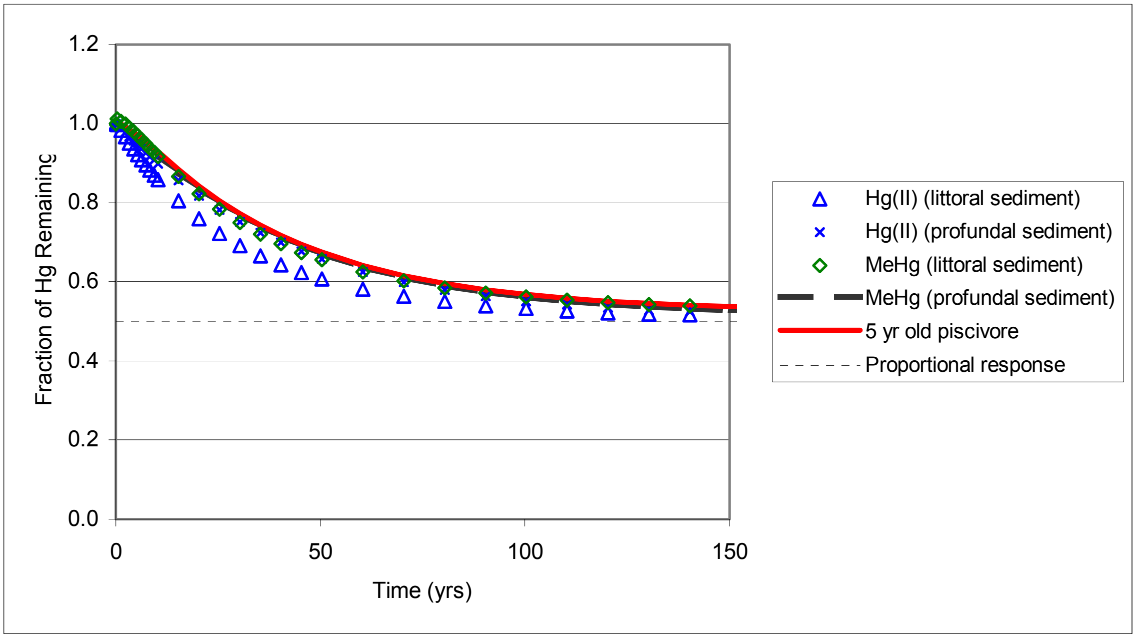


Figure 6-17
Predicted Fractional Responses to 50% Load Reduction in Pallette Lake (3 cm active sediment layer, 100% exchangeable inorganic Hg(II) in Sediments)

The base case scenarios for the four study lakes all used the assumptions that methylation occurs primarily in sediments, and that the sediment pool is 3 cm thick with all Hg(II) in the compartment being readily exchangeable. We wished to test some aspects of the predicted model response if most of the methylmercury supply to the lake was from other sources, e.g. water column methylation or external loading from streams. An additional simulation was run for Lake 240 with sediment methylation reduced to approximately 10% of it's original value and then increasing methylmercury loading in the inflow so that the total supply of in-situ production and external loading was equivalent to the base case scenario. External supply of Methylmercury now accounted for ~80 percent of the overall methylmercury load to the lake. In this scenario, all external loads or Hg(II) and methylmercury were instantaneously reduced by 50% and maintained thereafter at the lower rates. The predicted responses of methylmercury concentrations in various compartments are shown in Figure 6-18. Surface water methylmercury concentrations declined rapidly initially, while sediment concentrations were slower to respond. This is in contrast to the base case simulations where surface water methylmercury concentrations tended to follow the sediment methylmercury response with a time lag involved. This shows that if methylmercury production/loading is decoupled from the large reservoir of inorganic Hg(II) in the sediments then much faster methylmercury responses are possible in some compartments relative to others. The response of fish mercury concentrations would then depend on whether they ultimately obtain most of their methylmercury from the sediment or water-column pools as discussed in the next section.

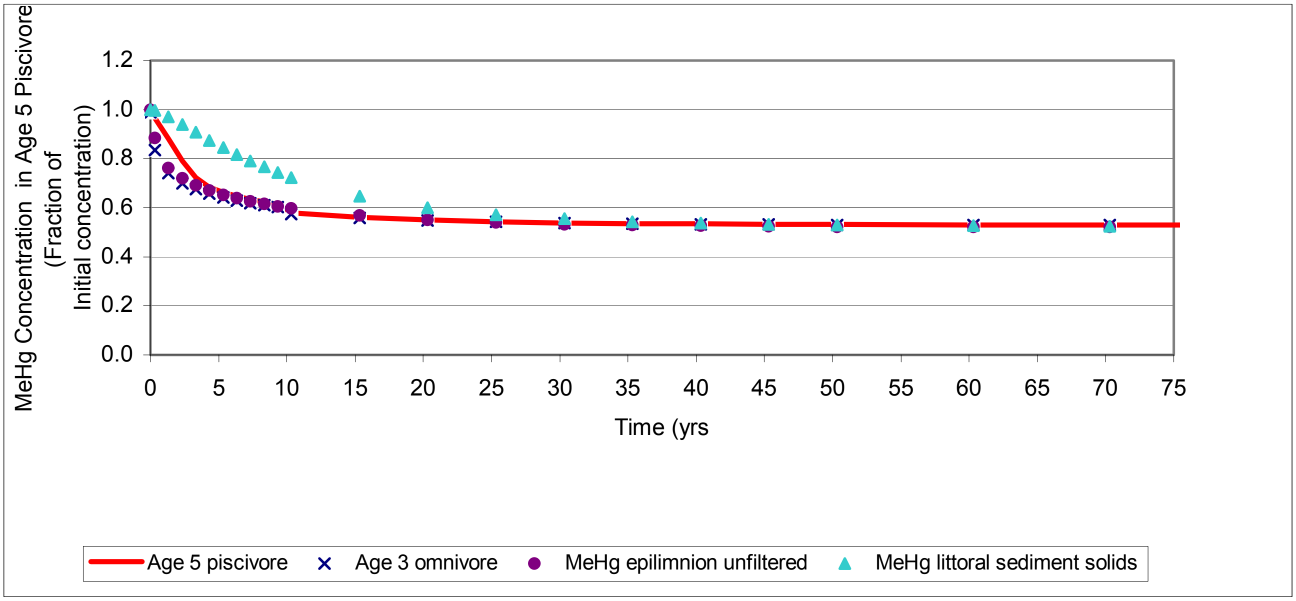


Figure 6-18
Predicted response of Methylmercury Concentrations in Lake 240 to an 50% Load Reductions – Alternate Scenario where 90% of Methylmercury Supply to the Lake is via Inflow

The Effect on Fish Response Times of a Benthic-Based Fish Diet

Two additional simulations were performed for Pallette Lake using different fish diets. The objective was to test if different fish mercury responses might emerge with pelagic-based versus benthic-based diets. In one simulation, benthos were effectively eliminated from the diet of all fish populations, forcing all the flow of "dietary" methylmercury to originate from the water column. For the second scenario, plankton were effectively eliminated from the diet of all fish populations, forcing all the flow of "dietary" methylmercury to originate from sediments. In both cases, the scenarios were run for 150 years following a 50% reduction in total mercury loading.

Figure 6-19 shows the dynamic predicted response of methylmercury concentrations in 5 year old piscivores in Pallette Lake for the base case calibration and the scenarios with benthic based or water column based diets. The results are normalized to the benthic methylmercury concentrations at the time the load reductions were invoked. Thus a value of 0.6 would mean the concentration was 60% of the value before the load reduction was invoked. The figure shows that whether the fish diet was primarily pelagic or benthic, the timing of the response of fish mercury concentrations was effectively the same, *for these particular scenarios*. Regardless of fish diets, both of these scenarios resulted methylmercury being supplied to the lake primarily from sediments, the slowest responding compartment in the model. The water column was able to respond relatively quickly to sediment methylmercury levels , and thus generally followed the same response trend. Thus it did not matter appreciably whether the fish ultimately derived their methylmercury primarily from the sediment or water column pools. If conditions existed however under which the responses of water column and sediment methylmercury concentrations were quite different (e.g. the example in Figure 6-18), the timing of the response of fish mercury concentrations could also be quite different, depending on the origin of most of their methylmercury (water column versus sediments).

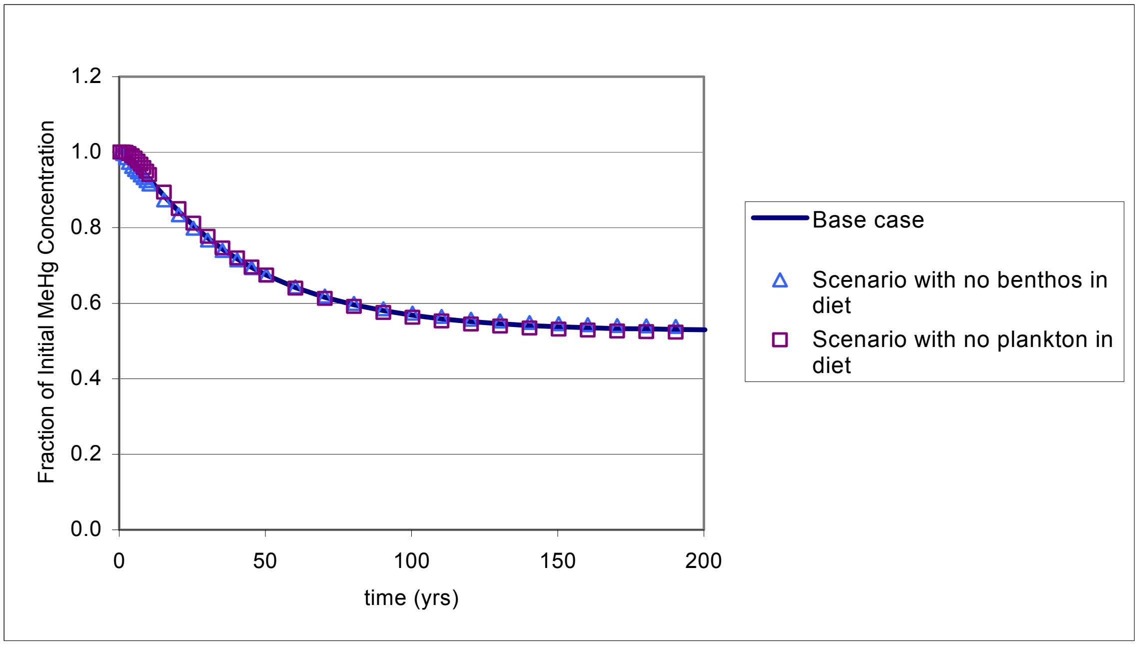


Figure 6-19
Effect of Benthic or Pelagic-based Diets on the Predicted Response of Age 5 Piscivores in Pallette Lake

7
DISCUSSION

Estimation of Selected Model Constants

The revised D-MCM calibrations in this report resulted in a reduced number of model constants that needed to be varied between lakes to obtain reasonable calibrations for the four lakes modeled. This means that the model is continuing to move towards a general predictive capability, but has not yet reached that stage.

Model Constants Related to Mercury Reactions

The rate constant for methylmercury photodegradation, Ksfac, was estimated from studies of methylmercury budgets done for Lake 240 (Sellers *et al*., 1996, 2001). The same value was applied to the four lakes, but in the absence of photodegradation rate estimates from other lakes, we were not able to test the general applicability of this rate constant and the model treatment of methylmercury photodegradation.

Photoreduction rates were adjusted using KsFacReduction so that when combined with elemental mercury produced by methylmercury photodegradation, the total annual production of elemental mercury approximated evasion estimates for Pallette and Little Rock Reference Lakes from Watras *et al*. (1994). Prior to this study, the inorganic Hg(II) complex assumed in D-MCM to be available for photoreduction in surface waters was $Hg(OH)_2$. However the predicted concentration of $Hg(OH)_2$ varies too widely across the pH range observed for natural lakes to generate plausible model results across this pH gradient. To moderate the sensitivity of the photoreduction reaction to pH, $HgCl_2$ and HgOHCl were also assumed to be available for Hg(II) photoreduction. This modification was made to obtain a better model fit to the often observed trend of lower surface water inorganic Hg(II) concentrations at higher pH, but does not have a strict scientific basis in terms of the actual complexes chosen to be photoreduced.

Even with the above changes to complexes being photoreduced, it was not possible to generate reasonable photoreduction rates and surface water inorganic Hg(II) concentrations for all four lakes, using a single value for the photoreduction rate constant (KsfacReduction). When the Hg(II) photoreduction constant calibrated from Pallette and Little Rock Reference Lakes was applied to Lake Barco, simulated photoreduction rates were excessive, probably by more than an order or magnitude, resulting in the underprediction of inorganic Hg(II) and methylmercury concentrations in surface waters. The overpredicted photoreduction rates in Lake Barco were likely due to the combination of high chloride concentrations which resulted in higher levels of two mercury-chloride complexes hypothesized available to photoreduce, together with very low

DOC concentrations in surface waters that allowed for greater light penetration in Lake Barco compared with the other three lakes modeled.

It is apparent that the current mechanistic representation of Hg(II) photoreduction in D-MCM needs to be modified in order to achieve general applicability. Several important factors affecting the process remain unknown, including the role of DOC in the process. It is not clear which complexes are photoreduced nor what range of wavelengths is involved.

A single value for the gross methylation rate constant in sediments was used for the four lakes (0.0176 ug methylmercury ug^{-1} Hg(II) available for methylation g^{-1} C decomposed). It is probably most appropriate however to think of these calibrations as providing a reasonable estimate of the overall supply rate of methylmercury to the lakes than as a calibrated measure of the actual methylation rate constant. This is because the predicted methylation rates in the lakes depend not just on the methylation rate constant, but also on the rates of carbon turnover, and the concentrations of Hg(II) that are available to be methylated. There is currently significant uncertainty in each of these terms in the model equation for methylation, and different combinations of the individual terms affecting methylation could potentially generate similar rates and trends.

In the case of the three seepage lakes, in-situ methylation is likely the dominant source of methylmercury to the lakes. The calibrated net methylation rates (gross methylation minus demethylation) may therefore be reasonable estimates of the net in-situ methylation needed to support observed methylmercury concentrations in those systems, assuming other methylmercury fluxes such as methylmercury photodegradation are also reasonably represented. The calibrated annual in-situ net methylation rates were 1.0, 1.3 and 0.5 ug m^{-2} yr^{-1} for Lake Barco, Pallette Lake and Little Rock Reference Lake respectively. For Lake 240, the combined supply rate of methylmercury due to inflows and in-situ net methylation was 0.9 ug m^{-2} yr^{-1}. Note that there is less confidence regarding the gross methylation and demethylation rates than the combined net methylation. This is because any number of combinations of gross methylation and demethylation rates may combine to generate a desired net methylation rate for a given site calibration.

Model Constants related to Mercury Partitioning

In terms of model constants related to mercury partitioning onto solid phases (e.g. water column suspended solids or sediment solids), D-MCM is not yet sufficiently predictive. Model constants had to be manually adjusted between sites and in some cases varied by more than an order of magnitude (e.g. partition constants for readily exchangeable inorganic Hg(II) and methylmercury on solids in littoral sediments, Appendix A). This is likely related to the variable nature of sediment solids in littoral zones in different lakes, which can range from sand to organic matter. One would expect different apparent mercury partitioning between the solid and filtered phases under such circumstances. The model does not have a mechanism in place yet to automatically accommodate differences in binding strengths for different types of solid substrates however. Furthermore, the model treatment of mercury complexation by sulfides is still under development. Sulfide complexation also affects the “apparent partitioning” between solid and filtered phases. More sulfide in solution would tend towards lower apparent partitioning onto the solid phase. Because of the above two limitations regarding the complexing strengths of solids and sulfides (where applicable), differences in partitioning constants have to be manually set between lakes. This is an area of model development that needs future attention.

Response Times of Fish Mercury Concentrations to Mercury Load Reductions

There are many steps in D-MCM linking a change in the rate of inorganic Hg(II) loading to the response of fish mercury concentrations (see discussion in Section 4). When considering changes in atmospheric mercury deposition rates, one must also consider the time required for changes in atmospheric mercury deposition to translate into changes in watershed mercury export in streams. Watershed mercury dynamics were beyond the scope of this study, and we focused on in lake (water, sediments, biota) mercury dynamics in this study.

Following imposed 50% reductions for external mercury supply rates in model scenarios, the predicted times to reach 90% of the long term response in 5 year old piscivores varied widely between the lakes (Table 6-11), even when all lakes were assumed to have 3 cm sediment layers and 100% readily exchangeable inorganic Hg(II) on sediment solids. Lake 240 was predicted to take 42 years to reach 90% of the long term steady state for age 5 piscivores, while Lake Barco was predicted to take 160 years. It is critical to note however that the Lake 240 simulation assumed an instantaneous change in stream runoff of inorganic Hg(II) and methylmercury following reductions in atmospheric mercury deposition. This is unlikely. It is quite plausible that the response of fish mercury concentrations in lakes receiving the majority of their inorganic Hg(II) and/or methylmercury from streams could be significantly delayed due to watershed mercury dynamics.

Even assuming an “instantaneous” watershed response to changes in atmospheric Hg deposition, the predicted response of the methylmercury concentrations in fish to inorganic Hg(II) load reductions was slow for all lakes (decades or longer) using base-case assumptions. Sediment inorganic Hg(II) concentrations were relatively slow to respond to changes in mercury loading to the lakes when the assumptions of a 3 cm sediment layer and 100% readily exchangeable mercury in sediments were applied. Thus the slow response of porewater inorganic Hg(II) concentrations translated into a slow response for methylmercury production rates in the lakes. Since in-situ production was the largest predicted source of methylmercur to the lakes, fish mercury concentrations also responded slowly. There were slight lags between the response of sediment inorganic Hg(II) and fish mercury concentrations (e.g. Figure 6-17), but the slow response of sediment inorganic Hg(II) was certainly a major contributor to the slow predicted response of fish mercury concentrations.

Two approaches were taken to examine the impact of the size of the pool of sediment mercury available for methylation on the dynamic response of fish mercury concentrations to mercury load reductions. The first approach was to consider a thinner sediment layer. The base case calibration assumed sediment layer of 3 cm. Reducing the active sediment layer to 1 cm essentially the amount of mercury stored in the sediments by two thirds. The second approach assumed that a portion of the inorganic Hg(II) in sediments was bound strongly to particles and therefore was not available for desorption and subsequent methylation, effectively removing it from the mercury pool available to methylate. The strongly adsorbed inorganic Hg(II) was released slowly with particle decomposition but much was buried before being recycled back into the “active” pool. The decomposition and release of strongly bound Hg(II) provided the equivalent of a minor background source of Hg(II) in the sediments when load reductions were imposed. Methylation was assumed to operate only on dissolved inorganic Hg(II).

The response of fish mercury concentrations was dramatically accelerated in all cases by modeling a 1 cm active sediment layer (Figure 6-13 through Figure 6-16). Fitted half-lives were reduced by as much as 60% compared to those predicted with the 3 cm simulations (Table 6-10). Improved response times for fish mercury concentrations were also obtained for Pallette Lake when 90% of the inorganic Hg(II) in the sediments was assumed to be strongly bound or irreversibly bound (Figure 6-13).

The fastest response times for fish mercury concentrations were obtained in Pallette Lake when the two approaches were combined, i.e. a 1 cm sediment layer with 90% strongly bound inorganic Hg(II) (Figure 6-13). Even faster responses could be expected by further reducing the active sediment layer and/or increasing the fraction of strongly bound inorganic Hg(II).

Table 6-12 shows the times predicted for 5 year old piscivores to reach 90% of the final methylmercury concentrations which would occur if the fish mercury concentration response was ultimately proportional to the reduction in inorganic Hg(II) loading, e.g. a 50% reduction in fish mercury concentrations for the 50% load reduction scenario. It is clear from the table that assumptions regarding the thickness of the active sediment layer and the nature of adsorption on sediment particles can have a profound effect on the predicted dynamic response of fish mercury concentrations using D-MCM. Each of these assumptions is discussed briefly below.

The appropriate sediment layer thickness to use is not well established. A first question is: What criteria should be used to set this depth? From the perspective of mercury cycling, at least two considerations emerge:

1. How deep is the layer from which methylmercury could be remobilized or accessed by the overlying system (including biota)? Many model studies assume an active sediment layer on the order of 2-10 cm. D-MCM simulations typically use a value of 3 cm.

2. How deep is the sediment layer in which methylation occurs? This is not well constrained either. It could be on the order of several centimeters or could be focused un the upper 1 cm (or less) near the sediment/water interface.

If the values appropriate for (1) and (2) above are different, it may be more appropriate to segregate the sediments into more than the one layer currently used in D-MCM.

Effects Of Pelagic And Benthic Diets On Fish Mercury Response Times

The predicted response of fish methylmercury concentrations in Pallette Lake simulations did not depend on whether the fish diet was primarily pelagic or benthic, under base-case assumptions with most of the methylmercury supply originating from a 3 cm deep sediment layer. This is clearly illustrated in Figure 6-19. In D-MCM, rapid steady state or equilibrium partitioning of methylmercury with the surrounding compartment is assumed for the lower food web compartments. Benthic methylmercury concentrations are assumed to be proportional to concentrations on sediment solids. Phytoplankton concentrations are modeled to effectively be proportional (rapid steady state) to concentrations of specific methylmercury complexes in the surrounding water. Zooplankton methylmercury concentrations are assumed to be directly proportional to phytoplankton. The predicted responses of methylmercury concentrations in the water column and the sediments were almost identical for the base case simulations . Consequently the responses of benthos and plankton were almost identical. It follows that the response times of fish mercury concentrations were not affected significantly by the mix of benthos and plankton in the diet, *for the base case scenarios in this study*. The key reason underlying this result is that most of the methylmercury in the four lake systems modeled in this study was calibrated to be supplied by sediment methylation. Since sediments are the slowest compartment to respond in the model system, the other compartments tend to follow the response of methylmercury concentrations in the sediments. Even though methylmercury concentrations were changing in the system as a whole for many years following mercury load reductions, there was a near steady-state balance in terms of methylmercury concentrations between the sediments and the overlying water column.

It should be noted that the choice of a pelagic versus benthic-based diet for fish could potentially affect the response dynamics of fish mercury concentrations under other conditions, as discussed below.

Predicted Methylmercury Response Dynamics When Most of the Methylmercury Supply is Not From Sediment Methylation

D-MCM has multiple compartments and multiple processes operating within each compartment. It is not necessarily always true that mass balance contaminant models will predict similar temporal responses in all compartments. Nor are predicted responses always amenable to being treated as simple exponential curves. As an example, a scenario was simulated for Lake 240, with inflowing streams providing 80% of the total methylmercury supply to the lake, and little in-situ methylation. When inflowing loads of inorganic Hg(II) and methylmercury were reduced instantaneously by 50%, concentrations of methylmercury and inorganic Hg(II) both declined quickly at first in surface waters, followed by a second slower recovery phase (Figure 6-18). A noteworthy point is that unlike the simulations discussed previously with methylation occurring in a 3 cm sediment layer, methylmercury concentrations in various compartments were predicted to follow quite different time courses for the scenario with most of the methylmercury supplied from stream inflows. For example, the response of methylmercury concentrations in sediments was predicted to lag that of the water column. The initial rapid decline of methylmercury in surface waters was due to the significant initial drop in the overall methylmercury supply rate to the water column, most of which was from stream inflows. The slower second phase of response was due to the effects of slowly changing supply of methylmercury from sediments back to the water column. In this scenario, no fish were assigned a benthic component to the diet. Age 3 omnivores were predicted to closely follow the 2-phase response of methylmercury in surface waters. Age 5 piscivores also responded quickly, but lagged the omnivores slightly. If the fish populations ultimately derived their methylmercury via a diet connected to sediment pool instead of water column, the fish would have been expected to follow a slower response, more influenced by the sediments. Thus the diet could be expected to potentially affect the response of fish mercury concentrations in situations where different underlying compartments are predicted respond at different rates. Comparable trends to this scenario could be expected for a situation where most of the methylmercury supply is from methylation in the water column, or at the sediment water interface if the reaction made use of "water column" inorganic Hg(II).

8
CONCLUSIONS AND RECOMMENDATIONS

D-MCM was recalibrated and applied to three seepage lakes and one drainage lake. The number of model constants requiring manual adjustment between the lakes was reduced, but some constants still needed site specific tuning on a site-by-site basis. This constrains the current predictive capability of the model and suggests that the treatment of some aspects of mercury cycling in D-MCM require modification. Specifically the Hg(II) complexes and role of DOC involved in Hg(II) photoreduction need to be clarified. For methylation and biological demethylation, the pools of Hg(II) and methylmercury that are available to participate in these reactions, and better estimates of true rates of methylation and biological demethylation, are needed. In terms of mercury partitioning, the kinetics of adsorption and desorption of Hg(II) and methylmercury needed to be better quantified, as well as the factors governing apparent partitioning between dissolved and solid phases.

Simulations were also carried out to test the effects of two assumptions commonly used in D-MCM simulations on the time required for fish mercury concentrations to respond to changes in mercury loading to lakes. These assumptions were that the sediment thickness layer should be 3 cm, and that all the inorganic Hg(II) on sediment solids is readily able to adsorb and desorb. Overall, the combined results of the simulations for the four lakes suggest the timing of the response of fish mercury concentrations to changes in external loading rates of inorganic Hg(II) is sensitive to the depth assumed for the sediment compartment and in some cases at least, the fraction of strongly bound inorganic Hg(II) on sediment solids. The slowest predicted fish mercury responses occurred with most of the methylmercury supply to the system originating from sediment methylation in a deeper sediment layer that has 100% exchangeable inorganic Hg(II) on sediment solids.

It was further found that the predicted timing of the fish mercury response to changes in mercury loading was also sensitive in some cases to whether the primary source of methylmercury supply to the system was sediment methylation, water column methylation, or inflowing stream loads. Shifting methylation to the water column is likely to produce faster responses of fish mercury to changes in mercury loading in situations when the fish ultimately derive a significant portion of their methylmercury burden from the water column pool.

It is important to note that the watershed could impose a strong influence on the timing of the response of fish mercury concentrations to changes in atmospheric deposition, for lakes receiving significant amounts of Hg(II) or methylmercury from streams. It is quite plausible that the response of the lake system to changes in atmospheric mercury deposition could be faster than that of the watershed. In such cases, the watershed response could dictate the long term response of fish mercury concentrations.

9
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A

MODEL CONSTANTS RELATED TO MERCURY PARTITIONING – MANUALLY ADJUSTED BETWEEN SITES

Table A-1
Coefficients for Partitioning onto Solids Used in Calibrations with all inorganic Hg(II) Freely Exchangeable.

Parameter	Units	Lake 240	Little Rock Reference Lake	Pallette Lake	Lake Barco
Inorganic Hg(II)					
K_Hg(II)_Solid (profundal sed)	$m^3\ g^{-1}$ (dry particle)	5.0×10^{10}	5.0×10^{10}	5.0×10^{10}	5.0×10^{10}
K_Hg(II)_Solid (littoral sed)	$m^3\ g^{-1}$ (dry particle)	1.0×10^{9}	5.0×10^{10}	8.0×10^{8}	5.0×10^{9}
K_Hg(II)_Solid (surface waters)	$m^3\ g^{-1}$ (dry particle)	8.0×10^{10}	5.0×10^{10}	8.0×10^{10}	5.0×10^{10}
Methylmercury					
K_methylmercury_ Solid (profundal sed)	$m^3\ g^{-1}$ (dry particle)	0.12	0.12	0.12	0.12
K_methylmercury_ Solid (littoral sed)	$m^3\ g^{-1}$ (dry particle)	0.12	0.12	0.004	0.004
K_methylmercury_ Solid (surface waters)	$m^3\ g^{-1}$ (dry particle)	2.0	2.0	2.0	2.0
Note: Partitioning of freely exchangeable inorganic Hg(II) onto solids is assumed to be proportional to the concentration of the free Hg^{++} ion in solution. Partitioning of methylmercury onto solids is assumed to be proportional to the concentration of the inorganic methylmercury in solution.					

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